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THE DESIGN AND CONSTRUCTION OF HIGH PRESSURE CHEMICAL PLANT

THE DESIGN AND CONSTRUCTION OF HIGH PRESSURE CHEMICAL PLANT

BY

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PREFACE.

THE object of this book is to describe personal experience of high-pressure chemical plant extending over many years, and to bring together the scattered sources of published information on this interesting and increasingly important subject.

Members of the staff of industrial organisations have attended from time to time at the Chemical Research Laboratory to gain knowledge of the design and construction of high-pressure chemical plant, and from my experience in this connection I have given prominence throughout the book to those aspects which appear to be of greatest practical value.

In the compilation of this work I have received considerable assistance from many sources, which I trust are adequately acknowledged in the text. My especial thanks are due to the Director of Chemical Research, Professor G. T. Morgan, O.B.E., D.Sc., F.R.S., for encouragement and help in the final arrangement of the subject-matter.

I am indebted to the Department of Scientific and Industrial Research and to H.M. Stationery Office for permission to make use of official records and to quote from official publications.

Finally, I must express my sincere thanks to my colleagues, Dr. G. R. Davies, B.Sc., Ph.D., who kindly corrected the proofs, and to Dr. H. Ingleson, M.A., D.Phil., for many translations from German literature.

TEDDINGTON,
January, 1934.

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CHAPTER I.

INTRODUCTORY.

ONE of the earliest recorded instances of the use of a pressure vessel for effecting a chemical operation is the digester invented in 1681 A.D. by Dionysius Papin, M.D., F.R.S., a Huguenot refugee who worked for some time in London with Robert Boyle. Papin used his digester for the extraction of marrow from bones, and he found that better results were obtained when the extraction was carried out under slight pressure. His apparatus is shown in Fig. 1. It consists of a bronze body and cover, which is secured to the body by means of a saddle clamp and screw. A very interesting feature of Papin's digester is the safety valve which is on the lever and weight principle, and Papin is popularly regarded as the inventor of this important fitting (Samuel Smiles—"Lives of the Engineers," "Boulton and Watt").

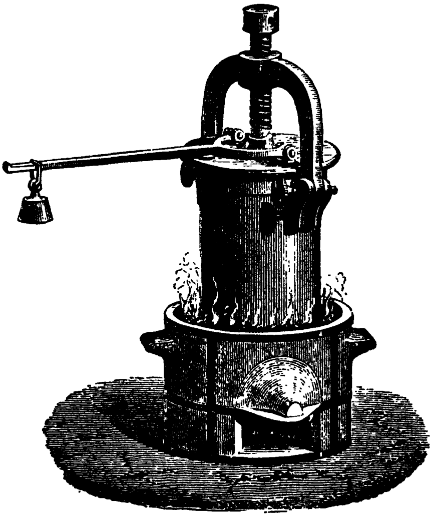

FIG. 1.—Papin's digester.

The early chemists employed sealed glass tubes for much of their work at low pressures. For example, Bunsen adopted this method in the preparation of cacodyl, and Frankland also used sealed tubes in his early preparation of zinc ethyl. Owing to the large quantities required, however, Frankland subsequently constructed a "digester" or autoclave with the assistance of Nasmyth, of Manchester, the well-known inventor of the steam hammer (Frankland, *Phil. Trans.*, 1855, **145**, 259).

This digester was made of Low Moor wrought iron, and was 18½ ins. long, with walls ⅝ in. thick, and 3 ins. internal diameter. The top was closed by a flanged cover ⅝ in. thick, into which was fitted a cast-iron thermometer pocket 6 ins. long × ½ in. internal diameter. Another opening in this cover flange was brass bushed and served as the seating of the safety valve, which, as in the case of Papin's digester, was on the lever and weight principle. The cover flange was secured to the body by means of four ½-in. bolts and nuts. The joint was made on a lead washer, and this was tight at pressures as high as 100 atms. Before being put into service, the vessel was tested by being filled to two-thirds of its capacity with water and gradually heated up to the melting-point of lead. Afterwards it was exposed to a more severe test, for on one occasion when charged with water and a glass tube filled with methylene iodide at a temperature of 200° C., the glass tube burst. Such was the tension of the methylene iodide vapour that the small safety valve (⅛ in. dia.) was instantly expelled and the heavily loaded lever thrown completely over.

This autoclave was used as a container for sealed glass tubes which contained the reagents. Liquid, usually water, was placed in the autoclave to surround the glass tube, so that in most cases the glass was under more or less balanced pressure conditions.

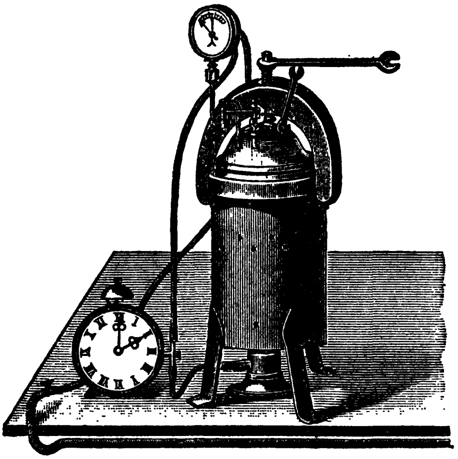

FIG. 2.—Laboratory autoclave, 1890-1900.

A second digester built by Frankland was made of wrought copper, being especially designed for the preparation of large quantities of organic zinc compounds without the intervention of glass tubes. It consisted of a wrought copper tube 18 ins. long, 2 ins. internal diameter, ½ in. thick, drawn from a solid mass of metal by a then recently invented process. The tube was closed at the bottom by a screw plug and fitted at the top with a flange, screwed upon the copper tube. The cover was secured to the body by three ½-in. bolts, and it was fitted with a stop-cock, so that if desired gas could be released from the apparatus.

A laboratory autoclave, built and marketed in Germany in the early years of the present century, is shown in Fig. 2. It is of mild steel, and differs but little in general appearance and design from that of Papin. In fact, such appliances were still known as digesters, and the term autoclave was but little used in connection with these laboratory pressure vessels.

In the industrial chemical field nothing of importance in pressure technique was developed until the middle of the nineteenth century, when the discovery of synthetic dyes by W. H. Perkin, Senior, in 1856, led to rapid improvements in really large high-pressure vessels. The subsequent need for considerable quantities of dimethylaniline, diphenylamine and similar aromatic bases was the cause of much activity in this field. The first of these amines was prepared by heating together aniline and methyl alcohol with a small quantity of sulphuric acid as a catalyst. The operation was carried out in cast-iron and steel autoclaves at temperatures of 230° C., and pressures of the order of 30-40 atms. were developed (G. T. Morgan, Hurter Memorial Lecture, *J.S.C.I.*, L, 104-109).

An example of an autoclave for operations such as the above, built in the years 1880-90 by Dietrich of Alsace, is shown in Fig. 3.

It is taken from Villon's book "Traité pratique des Matières colorantes artificielles," published by Librairie Polytechnique, Ch. Béranger, Paris, and I am indebted to the publishers for permission to reproduce it. It was of cast iron, and autoclaves of this type were made by Dietrich for pressures up to 100 atms., and capacities of 350 litres (about 80 gallons). The dimensions of the vessel are given in the drawing, from which it will be seen that the cover joint was made on the spigot and recess pattern, and the cover was secured by mild steel bolts. A stirrer was fitted, and these vessels were supplied with enamelled liners if desired.

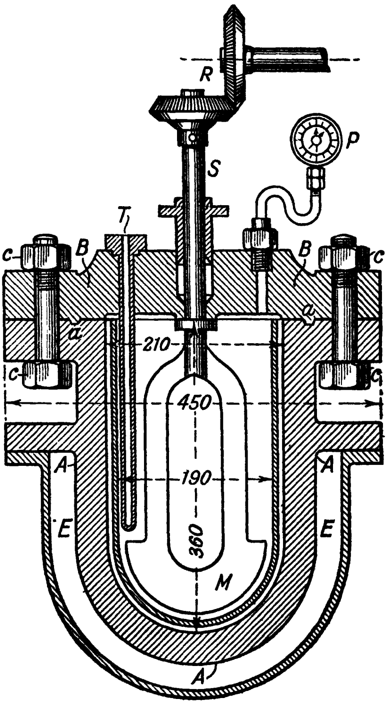

FIG. 3.—High pressure cast-iron autoclave, 1880-90.

An interesting summary of the manufacture of intermediates and dyestuffs at the beginning of the present century is contained in "Organic Colouring Matters," Schultz and Julius; edited by Arthur M. Green. (First published in 1894 and second edition in 1904, Macmillan & Co., Ltd.) From this summary it is apparent that a battery of high-pressure autoclaves is an essential feature of many branches of dyestuff manufacture.

The dyestuff industry in Germany was developed to a high degree of commercial and technical efficiency towards the end of the last century, and although the autoclave pressures employed were seldom higher than 60-70 atms., the experience gained in the fabrication and employment of such large pressure vessels was to be of great assistance to firms such as the Badische Anilin und Soda Fabrik when the work of Haber and his collaborators on the synthesis of ammonia under high-pressure-high-temperature conditions became industrially important.

The Synthesis of Ammonia.

The Haber process was, in fact, anticipated by Le Chatelier in 1901 (F.P. 313950), who caused hydrogen and nitrogen to combine at high pressure in contact with a catalyst. Unfortunately, a serious explosion wrecked his apparatus, and deterred him from making any further experiments. His results were confirmed by Perman (*Proc. Roy. Soc.*, 1905, **A**, **76**, 167).

Haber and his co-workers, commencing in 1904, studied the equilibrium between nitrogen, hydrogen and ammonia, using different catalysts and variations of pressure and temperature over a wide range (*Z. anorg. Chem.*, 1905, **43**, 111 ; **44**, 341 ; **47**, 42 ; *Ber.*, 1907, **40**, 2144 ; *Zeit. Electrochem.*, 1908, **14**, 181, 513).

With the co-operation and assistance of Dr. C. Bosch, who was responsible for the development of the Haber process on a commercial scale, the Badische Anilin und Soda Fabrik set up the first Haber-Bosch ammonia synthesis plant at Oppau between 1910-13, and the subsequent rapid increase in the output of this plant can be gauged from the following figures :—

Year.	*Approx. Production of* $(NH_4)_2SO_4$ *tons.*
1913	20,000
1914	60,000
1915	150,000
1916	300,000
1917	500,000

Since the war development of the Haber-Bosch process in Germany has been equally rapid. At the Leuna Works of the I.G. Farbenindustrie in 1923 the output of fixed nitrogen was 220,000 tons. This works employed then 11,000 labourers, 2500 craftsmen and 150 supervising chemists and engineers (Ernst, " Fixation of Atmospheric Nitrogen," 1928, Chapman & Hall, Ltd.).

The Oppau Works of the I.G. Farbenindustrie has now (1933) a capacity of 100,000 tons of fixed nitrogen, and the Leuna works about 500,000 tons of fixed nitrogen annually, and the staff engaged on the fixed nitrogen plants at both works now reaches the huge total of 40,000 persons.

At the Billingham works of Imperial Chemical Industries Ltd. the output of fixed nitrogen per year is of the order of 200,000 tons.

The synthesis of ammonia is represented by the equation

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + \begin{cases} 28{,}000 \text{ cals. (Nernst)} \\ 24{,}000 \text{ cals. (Haber-Berthelot).} \end{cases}$$

The heat of the reaction is used in the various synthetic processes to maintain the required temperature of the catalyst.

Ammonia can, of course, be synthesised at ordinary pressure, but the yield is so small as to be impracticable from a commercial aspect. Increasing the pressure favours the combination of nitrogen and hydrogen, while increasing the temperature favours dissociation of ammonia. These points are brought out quite clearly in the following curves (Fig. 4) (Larson, "The Ammonia Equilibrium at High Pressures," *J. Amer. Chem. Soc.*, 1924, **46,** 367-372).

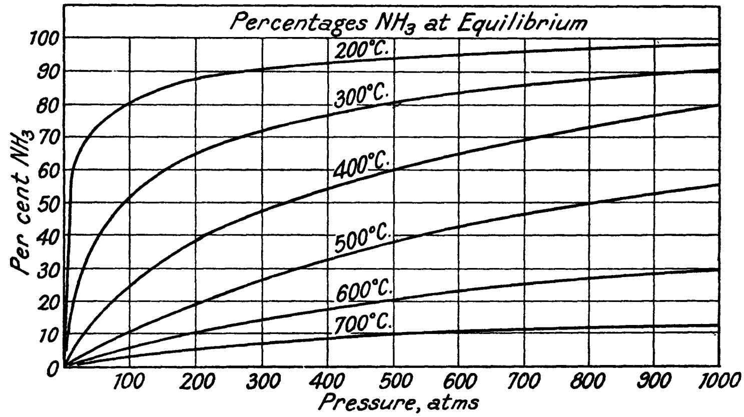

FIG. 4.

The pressures employed in the actual manufacture of synthetic ammonia vary from 100-1000 atms., and a reaction temperature of 400-600° C. Even under these conditions the synthesis is only possible with the use of a catalyst, which in all cases is essentially metallic iron (M. R. Applebey, *Proc. Roy. Soc.*, 1930, **A, 127,** 256). Many other substances have been proposed as catalysts, and almost every element in the periodic table has been patented at one time or another, but iron is the one substance which is used on a large scale for the ammonia synthesis.

Pure iron is initially a very active catalyst, but its activity soon declines. The addition, however, of quite small percentages of magnesia or alumina renders the catalyst practically permanent, provided due precautions are taken to remove " poisons " from the reacting gases. Oxygen and oxygen compounds, for example, are most poisonous, and very great care is necessary to exclude these from the synthesis plant.

In nearly all synthetic ammonia processes the nitrogen required is obtained directly from the liquefaction of air, or indirectly by the removal of oxygen from air by combustion, and the hydrogen is obtained from coke oven gas, water gas, producer gas, or from the electrolysis of water. The last method is only practicable when electric power is very cheap.

The original Haber-Bosch process involved a working pressure of 200-250 atms., and reaction temperatures of 500-600° C. (Haber, E.P. 14023 of 1910; D.R.Pp. 229126, 238450 of 1909; U.S.P. 971501 of 1910). The hydrogen-nitrogen mixture for the Haber-Bosch process is obtained from a mixture of water gas and producer gas. Air is burned with coke to give producer gas, which is mixed with water gas obtained by the interaction of steam and red-hot coke, and the mixture passed with excess of steam over an activated iron oxide catalyst. If suitable relative quantities of water gas and producer gas are used initially, the resulting gas, after removal of carbon dioxide, etc., consists of nitrogen and hydrogen in the proportions approximately 1 : 3 and is used after final purification for the synthesis of ammonia.

Under the conditions of the Haber-Bosch process, a theoretical conversion of about 13 per cent. per catalyst contact is possible, and in practice the conversion reaches about 8 per cent. In operation the withdrawal of nitrogen and hydrogen as ammonia leads to undesirable accumulation of inert gases, such as methane and argon in the circulatory system. This is avoided by regulated discharge of the gases, whereby some 10 per cent. of the circulatory gases are rejected. This purge keeps down the proportion of inert gases to below 5 per cent.

The first catalyst tubes used in the Haber-Bosch process were of mild steel externally heated, but this design was quickly abandoned on account of the action of hot hydrogen and ammonia on the steel walls of such vessels. Early devices to avoid this included surrounding the catalytic furnace in a large envelope containing nitrogen at the pressure of the interior of the catalyst chamber, but this was not very effective. All recent types of catalyst tube are constructed of alloy steels, and the tubes are specially designed to prevent weakening of the shell by gas penetration and corrosion. Details of such appliances will be found in Chapter IX.

The other important high-pressure synthetic ammonia processes are the Claude, the Casale, and the Mont Cenis. These differ from the original Haber-Bosch process in details such as the working pressure and temperature. The Claude process is particularly noteworthy because of the high pressure employed (900-1000 atms.). The Casale process uses a working pressure of 750 atms., and the Mont Cenis 100 atms.

Details of these plants, and also of the Haber-Bosch process, will be found in Chapters III. and IX.

It will be realised that such severe working conditions have proved quite troublesome in the early stages of development, but thanks chiefly to recent great advances in the metallurgical art, the initial difficulties have been surmounted, and such plants are now almost monotonously reliable in operation.

It is obvious that the phenomenally rapid growth of these synthetic ammonia processes must necessarily have had far-reaching effects of an economic character. The following brief résumé of a few of the effects of this new industry will serve as illustrations in this respect :—

In 1913 about 55 per cent. of the world's nitrogen was supplied by nitrate of soda, chiefly from Chile. In 1923 the amount obtained from that source had decreased to 32 per cent., owing to competition from the synthetic ammonia industry, and during the past 10 years the diminution of the proportionate supplies from Chile has been even more marked. The average price of sulphate of ammonia in New York during the year 1913 was $3.14 per 100 lbs., whereas in 1928 the prevailing price was $2.35 per 100 lbs., in spite of the fact that commodity prices generally were 50 per cent. higher than in 1913 (*Proc. 2nd Int. Conf. Bituminous Coal*, 1928, **2**, 170).

Although the price of Chile saltpetre has been considerably reduced, and assistance given to this industry by State subsidies, it is becoming increasingly difficult for it to compete against synthetic ammonia in the world nitrogen market. There is little doubt that the recent unhappy series of revolutions in that country are due in no small measure to the general depression in its commercial life as a result of the diminishing importance of the once prosperous Chilean nitrogen industry, which has the huge capital of £75,000,000 (*Chemical Trade Journal*, 1933, **92**, 5).

Large commercial gas undertakings in the British Isles are also confronted with a similar problem. Sulphate of ammonia was once a very favourable by-product in these undertakings, and it played no inconsiderable part in the profit and loss account. The synthetic ammonia industry has dealt the gas-making concerns a serious blow in this matter. This will be apparent from the following brief extract from the speech of Sir David Milne Watson, at the annual general meeting of the Gas Light and Coke Co., Ltd., held on 10th February, 1933 :—

> "It is sad to see sulphate of ammonia producing a loss. In the past we have made £200,000-£300,000 profit from the product, but this year you will see that we have made a loss of £4000."

The importance of the arc and cyanamide fixed nitrogen processes is also steadily diminishing as a result of the growth of the high-pressure synthetic ammonia industry, and the former are quite unable to compete in many localities. I do not think the most sanguine of the directors of the B.A.S.F. ever dreamt that their courageous efforts in 1909-13 would have such far-reaching financial and political effects.

The technique acquired in the development and operation of these high-pressure synthetic ammonia plants has turned the attention of chemists and chemical engineers to other branches of the chemical industry where high pressure might profitably be applied, and where the experience gained on the ammonia plants could be put to immediate use.

Perhaps the most successful of these new developments of high-pressure chemistry have been the syntheses of methyl alcohol from carbon monoxide or carbon dioxide and hydrogen, and urea from carbon dioxide and ammonia. In the former case the operating conditions are 200-300 atms., and catalyst temperatures of 390-425° C., whereas in the case of urea the pressure employed is 100 atms., and the temperature 150° C. (*Chem. Met. Eng.*, 1930, **37**, 530).

The Synthesis of Methyl Alcohol and Urea.

The synthesis of methyl alcohol is represented by the following equation—

$$CO + 2H_2 \rightleftharpoons CH_3 . OH + 27{,}200 \text{ cals.}$$

Hence, as in the case of ammonia, the production of methyl alcohol is favoured by increased pressure, and by diminishing temperature, the latter, of course, consistent with a practicable conversion rate.

The first suggestion to employ water gas (carbon monoxide and hydrogen) as a source from which to manufacture methyl alcohol is contained in the Badische Patent, D.R.P. 293787, and British Patent 20488, both granted in 1913, and by 1923 this firm was undoubtedly manufacturing methyl alcohol by this process on a commercial scale. It is due, however, to the published researches of Audibert and Patart (Patart, *Chim. et Industrie*, 1925, **13**, 179; 1926, **16**, 713, and Audibert, *ibid.*, 1925, **13**, 186, and later, for example, by Morgan, Taylor and Hedley, *J.S.C.I.*, 1928, XLVII., 117, and Wèttburg and Dodge, *Ind. Eng. Chem.*, 1930, **22**, 1040), that full details of the methyl alcohol synthesis have been made available.

As in all similar cases, innumerable patents have been granted for catalysts in the preparation of methyl alcohol from carbon monoxide and hydrogen. The most successful catalysts appear to be basic zinc chromate and zinc oxide. The temperature normally employed is 390-425° C., and the pressure 200-300 atms., when with the above catalysts quite good yields of nearly pure methyl alcohol are obtained (F.P. 599588, and the corresponding English Patent of 1925, 252361). At the present time, investigators all over the world are endeavouring to produce alcohols higher than methyl by varying the gas mixtures, temperatures and notably the catalyst (e.g. Morgan and Taylor, *Proc. Roy. Soc.*, 1931, **131A**, 533).

As an example of the growth of synthetic methyl alcohol production, the output in the U.S.A. by this process was 500,000 galls. in 1927, whereas in 1930 this had risen to the huge figure of 10,000,000 galls. (*Chem. Met. Eng.*, 1930, **37**, 530).

An interesting development in the synthesis of methyl alcohol is the process used by the Commercial Solvents Corporation at Peoria, Ill., U.S.A. A by-product of the fermentation of corn to produce acetone, etc., is a large volume of gas containing 40 per cent. of hydrogen and 60 per cent. of carbon dioxide by volume. In 1925 the gas was used as a fuel, and the return from this employment was naturally low, but by utilising the synthetic methyl alcohol process, involving pressures of 300 atms., and a temperature of 400° C., a good yield of methyl alcohol is obtained. The original gas is, of course, too rich in carbon dioxide to be used directly in the methyl alcohol synthesis, so a proportion of this gas is removed by washing with water under pressure. The carbon dioxide thus removed from the synthetic process is piped to a branch of the Dry Ice Corporation, to be made up into blocks of solid carbon dioxide for use as a refrigerant (*Chem. Met. Eng.*, 1930, **37**, 548).

Urea is synthesised by interaction of carbon dioxide and ammonia at pressures of 100 atms. or so, and temperatures of the order of 150° C. This substance is made in large quantities at the Leuna works of the I.G., and autoclaves are used for the process. Its chief use is as a highly concentrated fertiliser for valuable crops, such as vine, tobacco, tea, etc.

Hydrogenation of Coal.

Another very important development of the application of pressure to facilitate chemical change is the hydrogenation of coal and carbonaceous material by what is now generally known as the Bergius process. The hydrogenation of coal may be said to date from the investigations of Berthelot who some 50 years ago used concentrated hydriodic acid as a catalyst, but it was not until 1913 when Bergius made the announcement that, at hydrogen pressures of 200 atms., and a temperature of 400-500° C., coal could be converted into a tar-like oil that the subject became of industrial importance. Since that date, investigators all over the world have devoted a considerable amount of time and money in the hope that such a process would eventually become a serious rival to the established natural petroleum interests.

On the occasion of the Bituminous Coal Conference held in Pittsburgh, U.S.A., in 1926, the pioneer of this process, Dr. Friedrich Bergius, gave details of the large amount of research work carried out by himself and his co-workers on this important subject. Some idea of the enormous cost of this research can be gathered from the statement by Herr Bruchmann, President of the Erdol und Kohlenverwertungs, A.G., that during the period 1913-28, the total cost had been 28,000,000 gold marks.

Recently an international organisation, which includes the Imperial Chemical Industries of Great Britain, the Standard Oil Company of U.S.A., and the I.G. Farbenindustrie of Germany, has been formed to hold the many patents in connection with the Bergius process. Whilst the European members of this group have confined their attention to the hydrogenation of coal, coal tar, lignites, etc., the American concerns have devoted their energies to investigating the value of this process in the handling of petroleum (*Trans. Inst. Chem. Eng.*, 1931, **9**, 145).

A considerable amount of information about the Bergius process for the hydrogenation of coal, etc., is contained in a recent paper by Ormandy, and also in the subsequent discussion (*Trans. Inst. Chem. Eng.*, 1931, **9**, 107). Dr. Ormandy reviewed in considerable detail the position of coal from the national standpoint in Great Britain, and the following abstract is of considerable interest in so far as the hydrogenation of coal is concerned.

In the first place, the total importation of oil into Great Britain during the past few years has been as follows :—

	Million gallons.
1921	1,161
1926	1,916
1927	2,051
1928	2,108
1929	2,195
1930	2,405

This can be divided up into

	Million gallons.	
	1929	1930
Motor spirit	810	955
Fuel oil	114	131
Gas oil. . . .	406	491
Crude oil	487	461

Remainder—Lubricating oil, etc.

Of the crude oil, about 30 per cent. was distilled, and motor spirit and other products obtained from it.

With the exception of comparatively small quantities of benzole produced from the distillation of coal, and small quantities produced in the Scottish Shale Oil Industry, this country is entirely dependent upon importations for its supply of motor spirit and oils. Due to the world-wide over-production of oil, the price of petrol at Thames Haven (No. 1 quality) in bulk has been as low as 2½d. per gallon.

Bituminous coal consists essentially of carbon, hydrogen and oxygen with small quantities of nitrogen, sulphur and other bodies. The hydrogen content of bituminous coals ranges from 4½-5½ per cent. Mineral oil is much richer in hydrogen, as it contains about 15 per cent., and hence the hydrogenation of coal to produce oil involves the addition of roughly 10 per cent. of hydrogen on the weight of the coal. Bearing in mind the figures just quoted for petrol, viz. 2½d. per gallon, it will be realised that cheap hydrogen is essential to such a process, since to convert a quantity of coal into a ton of petrol means roughly 40,000 cu. ft. of gas.

In the first experiments carried out by Bergius, that is until 1924 or so, a discontinuous autoclave type of plant was used, and many thousands of experiments were carried out in these appliances, although quite a large continuous plant was at work on the hydrogenation of heavy oils. In 1924 the first continuous plant for the hydrogenation of coal came into being. In the early continuous plant experiments a product called Luxmasse was added to the coal oil mixture to combine with the sulphur always present. It was then specifically stated that the hydrogenation process as developed by Bergius was a direct combination carried out without added catalyst. (The Luxmasse used was the residue left after extracting alumina from bauxite, and consists essentially of iron oxide.)

The advances made in the Bergius process of recent years have been firstly in the development of catalysts and promoters which assist catalytic hydrogenation, and improvement in plant design to eliminate the early troubles due to hydrogen penetration and corrosion. In the early work such plant troubles were most serious, and even now they constitute one of the most important technical problems.

The coal selected for hydrogenation treatment was ground to the same degree of fineness as is customary in pulverised fuel furnace work, and the finely divided coal in the dry state was mixed with about 40 per cent. of its weight of the heavy oil produced by an earlier operation, and to this paste was added the desired amount of Luxmasse. After mixing this paste was pumped by specially designed hydraulically driven paste pumps into a heated vessel through which hydrogen was passing at pressures from 150 to 200 atms.

These reaction vessels were externally heated by gas flames and the contents agitated by means of rotating scrapers. At the end of the reaction vessel the comparatively thin fluid-like product was discharged through a valve into a receiver where the liquid was separated from the gas. Although considerable improvements in technique and design of plant have been made during the past nine years, the fundamental principle of the Bergius process remains the same.

It is interesting to calculate the coal requirements in connection with the Bergius process. It may be assumed that for every 1⅔ tons of coal passed through the reaction vessels, approximately 2⅓ tons are necessary for all other purposes. So that to make 1 ton of petrol requires 4 tons of coal, and since our petrol requirements amount to 3,500,000 tons per annum, approximately 14,000,000 tons of coal would be required. In view of recent developments in the use of Diesel and heavy oil engines for vehicle propulsion as an alternative to petrol engines, it is possible that more heavy fuel oils will be required. Fortunately, from this point of view, the Bergius process is able to produce a wide variety of fuel oils, depending upon the conversion conditions.

A very interesting contribution to the discussion on Dr. Ormandy's paper was made by Mr. Gordon of Imperial Chemical Industries, in which he gave details of the work being done by that organisation.

Mr. Gordon stated that in Germany a plant had been constructed to produce 100,000 tons of petrol from brown coal per year, and in America two large plants had been built for the hydrogenation of crude oils. At the Billingham works of Imperial Chemical Industries Ltd., there was a pilot coal hydrogenation plant which was capable of dealing with 15 tons of bituminous coal per day, and which had been in operation over two years. His company were prepared to build a plant of whatever size desired which would operate in accordance with plan. Schemes had been prepared for plants to treat 1000 tons of coal per day and produce 210,000 tons of petrol per year. Such a plant, allowing for all contingencies, working capital and interest during the construction period, would cost £8,000,000. Only about one-quarter of this expenditure represented items which were novel. The estimated cost of petrol produced by this plant, including obsolescence, was 7d. per gallon, compared with the present imported price of 2½d. per gallon.

An interesting forecast of recent events in this country is provided by the following extract from the speech by Sir H. McGowan at the annual general meeting of Imperial Chemical Industries held on 11th April, 1933 :—

> "We have continued our research work on hydrogenation with marked success. Much has been written on the economics of the process. These comments have necessarily been based only on costs, etc., which I myself made public some 18 months ago, and do not make due allowance for the great strides since made.
>
> "Our technical staff is still working on the direct hydrogenation of coal. We are satisfied that this is the correct policy. It does not preclude the use of tars as they become available in suitable quantity and at suitable prices, and we foresee a definite field for tar hydrogenation as well.
>
> "Large-scale development of our hydrogenation process now only awaits upon progress in regard to a limited number of economic factors. When that is achieved we shall be prepared to invest a substantial sum out of our present liquid resources upon this enterprise."

On Monday, 17th July, 1933, the Prime Minister (Mr. MacDonald) stated in the House of Commons that home-produced motor spirit would be assisted by a preference of fourpence per gallon for a stated period of years. This was followed a day or two later by the following official statement issued to the Press by Sir H. McGowan, Chairman of Imperial Chemical Industries :—

"For six years Imperial Chemical Industries Ltd. have conducted research on the hydrogenation of coal, tar and other materials.

"In view of the undertaking given in the House of Commons by the Prime Minister, the directors of Imperial Chemical Industries Ltd. have now authorised a scheme for the erection of a large commercial plant, which is to be located at the company's works at Billingham-on-Tees, Co. Durham, where special facilities are available.

"An initial output of 100,000 tons a year of first-grade petrol is aimed at by processing 400 tons of coal a day, and using altogether about 1000 tons of coal a day.

"The operation of the plant will give permanent direct employment to 2500 miners and other workers, as well as much indirect employment.

"The construction of the plant itself, estimated to take about 1½ years, will call for much activity in the iron and steel and heavy industries. Seven thousand men will find direct employment during these 1½ years, and it is expected that there will be indirect employment for a further 5000 men.

"The necessary new capital of about 2½ millions sterling will be furnished by I.C.I. Ltd. from their own resources, which are ample for this new enterprise and for the general business of the company."

At the recent World Petroleum Congress held in London during July, 1933, Mr. K. Gordon, of Imperial Chemical Industries, gave a very interesting paper on the subject of the hydrogenation of bituminous coal, and I am indebted to the Congress for permission to publish the following extensive abstract :—

Hydrogenation in England has from the beginning been primarily concerned with bituminous coal and the by-products of coal distillation, and as far as can be foretold this will always be the position. While no commercial plant for the hydrogenation of bituminous coal is yet in existence, the advance in knowledge and technique during the last decade has been very great, so that from a position of relying entirely on imported knowledge, we now in Great Britain are the authorities on the production of hydrocarbon mixtures from bituminous coal, and the design of large-scale plant to accomplish this production.

Coal hydrogenation is essentially different from destructive hydrogenation of a heavy hydrocarbon material such as crude petroleum. Although the weapon used, hydrogen at high pressures, is the same, the reactions involved are entirely different, for the problem really resolves itself into that of the treatment of ulmin compounds, in the molecule of which oxygen may be regarded as the key element.

Effect of Hydrogenation.

It can now be seen that the functions of a hydrogenation process to produce a light hydrocarbon oil from coals must include :—

(*a*) Reduction of the oxygenated groupings of the ulmin compounds and removal of sulphur and nitrogen before thermal decomposition can set in at these weak points of the molecules.

(*b*) The resulting high molecular weight product of low hydrogen to carbon ratio must be broken down and hydrogen added by a combination of cracking and hydrogen saturation to give a mixture of liquid hydrocarbons of low molecular weight, and comparatively high hydrogen to carbon ratio.

(*c*) A means for the continual purging of ash and unchanged or partially changed solid from the system.

Actually, it is found that, with the majority of British coals, the hydrogenation reaction can be so catalysed that the preliminary reduction takes place extremely rapidly. It is therefore possible to confine the preliminary reduction and subsequent destructive hydrogenation reactions to one liquid phase process. With an appropriate catalyst, reduction of a coal can be brought about under pressure at temperatures as low as 300° C., while destructive hydrogenation is not appreciable below 400-420° C.

Variation of Conditions.

The extent to which destructive hydrogenation occurs depends mainly on the reaction temperature, reaction time, catalyst, and pressure of hydrogen. By variation of these conditions a coal can be converted either into petrol, intermediate middle oil, gas, and 3-5 per cent. solid organic residue, or, with extremely mild conditions, into a mixed oil product consisting mainly of heavy oil. Increase in yield of solid organic residue imposes a limit to the mildness of a possible treatment.

In practice continuous injection of dry coal into a pressure plant is unsatisfactory, and the feed material always consists of a paste of coal and oil. The oil in this paste also undergoes destructive hydrogenation, so that, by suitable control of the variables enumerated above, three types of liquid-phase processes can be carried out :—

(1) Tar or heavy oil from an external source may be used as pasting oil, and the paste of coal and tar hydrogenated in a single stage into petrol and intermediate middle oil.

(2) The pasting oil can be wholly recycle oil from the process itself when the net effect is that the coal only is converted into petrol and middle oil.

(3) The employment of milder conditions than in (2), when the coal may be converted into a mixture of heavy oil, intermediate middle oil, and petrol. The heavy oil may be marketed as a fuel oil, or hydrogenated separately under its particular reaction conditions to give a lighter oil product.

The influence of the variation of these reaction conditions has been extensively studied in semi-technical plants capable of treating 3-8 cwts. of coal per day. An experiment under any one set of conditions is run continuously for not less than a week, and is divided up into 12-hour test periods. Over each period a balance of reactants and products is obtained by measurement and analysis of the hydrogen, hydrocarbon gas, middle oil, heavy oil, solid organic matter, aqueous liquor and ash, fed to and produced from the plant. The results are expressed in terms of the quantity of newly formed petrol, gas, etc., as a percentage of the make-up feed. Typical yields from 100 parts of British bituminous coals are given in the following table : A. For a process designed to give petrol and middle oil only. B. For a process worked to give heavy oil, middle oil and petrol :—

	A.	B.
Petrol	31·3	14·0
Middle oil	37·3	32·2
Heavy oil	5·0	32·2
Gas	23·6	15·3
Organic insolubles	3·0	3·0
Liquor	9·6	9·8
Hydrogen absorbed	9·8	6·6

Variations with Different Coals.

It may be stated at the outset that, by suitable choice of conditions, good yields of light oil have been obtained from all British coals tried, with the exception of anthracites. To determine the conditions for these good yields there has had to be extensive experimentation over a long period in continuous experimental plants in which the suitability of coals for hydrogenation has been assessed by determination of the following :—

(*a*) Time of reaction required for a given extent of hydrogenation.
(*b*) The ultimate yield of petrol obtainable.
(*c*) The quantity of hydrogen required per unit of petrol.
(*d*) The necessity for modification of the catalyst conditions.

The results of this work have shown, as would be expected from what is known of coal constitution, that the composition of the ulmin compounds largely determines the suitability of a coal for hydrogenation, and it is therefore now possible to obtain an estimate of the yields, etc., obtainable from a coal, by examination of its ultimate analysis. Such estimates are often valueless in the range of 86-88 per cent. carbon coals, since in this range many of the other general relationships between carbon content and coal properties frequently break down. Theoretically, the higher the carbon content of the coal, the greater would be the ultimate petrol yield, and since coals with high carbon content have approximately the same hydrogen content with a smaller oxygen content than low carbon coals, the hydrogen absorbed per unit of petrol produced should be lower. In practice, however, it is found that the reaction volume required increases with increasing carbon content as do the yields of hydrocarbon gas and insoluble residue, and the balancing of these factors is only one of the complicated economic problems which have to be evaluated in considering the choice of a site for a commercial plant.

With regard to the influence of other coal constituents, variable contents of hydrocarbons and resins have little effect on the suitability or otherwise of coals. A coal having a high content of vitrain is more suitable than dull coal, although this is probably not so much due to the plant entities as to the presence in durain of a more difficultly hydrogenable ulmin compound.

Large-scale Design.

The technical design of large-scale plants is a problem demanding full knowledge of all research results on the hydrogenation of coal, and of the most advanced high-pressure technique. Imperial Chemical Industries Ltd., therefore, started the design of large-scale plants immediately research results of any value were obtained, and its design has been continuously revised as research or engineering developments showed possible improvements. All the details consist of parts that have been tested on the small scale at Billingham, on the large scale in Germany, or are standard pieces of oil equipment, while the design as a whole can be considered as the most thoroughly developed and advanced design for any high-pressure plant existing or in design to-day.

Special high-pressure pumps for injecting the coal-oil paste have been fully proven. This paste with high-pressure hydrogen is then heated to the reaction temperature in interchangers followed by gas-fired heaters somewhat similar in design to standard oil heaters. The reaction vessels are vertical special steel cylinders which liners protect from any corrosive attack of hydrogen and sulphur. Thermal circulation and the hydrogen maintain stirring of the burden without mechanical aid.

The products are removed from separators maintained at such temperatures as will reduce distillation without complication of the system. In these separators the gas from the converters is separated from the oils and passes on to a washing plant where the excess hydrogen is washed free of the hydrocarbon gases formed in the reaction and can be circulated back to the converters.

The oils before distillation are let down from the reaction pressure in various stages to recover light hydrocarbons most effectively and produce stable oils.

The ash and organic insolubles are retained in the hottest separator and, after letting down, are separated from the oils, which were also in this separator, by centrifuging. The cake still contains some oil which can be distilled off from the solid.

Vapour-phase Hydrogenation.

Low molecular weight products formed in liquid-phase hydrogenation are swept rapidly out of the converter by the stream of hydrogenating gas, and there is consequently little opportunity for the hydrogen to convert them further into petrol. In addition, the liquid-phase catalyst which is added continuously in small amounts to the coal paste has little chance of contact with the vapour-hydrogen bubbles passing through the liquid reactants.

These low molecular weight products are obtained from the bulk of the products as distillate oils boiling above 170° C. and below 300-320° C., and are hydrogenated to give a further yield of petrol by passing a mixture of the oil vapour and hydrogen under pressure over a fixed catalyst. The oils consist of a mixture of phenols, bases, sulphur compounds, and aromatic hydrocarbons which give poor yields of petrol when cracked, but high yields when hydrogenated in the presence of a suitable catalyst. Over all these hydrogenation catalysts the phenols, bases and sulphur compounds are reduced to the corresponding hydrocarbons, the catalysts being completely resistant to sulphur poisoning.

The quality of the petrol required determines the exact temperature for the reaction and the catalyst which must be used, but all these reactions must be at a temperature sufficiently high for the oil to be completely vaporised in the stream of hydrogen. There must be regulation between temperature, pressure and catalyst activity to give the proper balance between hydrogenation and cracking. In the cracking of such an oil as this, the polycyclic aromatics would be decomposed into molecules which would readily condense to higher molecular weight compounds, and the hydro-aromatics would be dehydrogenated. The high pressure of hydrogen in the vapour-phase hydrogenation prevents any condensation and displaces the equilibrium at the lower temperatures away from the production of aromatic hydrocarbons towards the formation of hydro-aromatic hydrocarbons. The production of the lower-boiling simple aromatics from the polycyclic aromatics is probably through saturation and subsequent opening of an outer ring.

The addition of the hydrogen is a very marked exothermic reaction and the lower the temperature the more saturation of the aromatic rings takes place. This dependence of the nature of the final product upon temperature adds to the importance of the catalysts, but when the catalysts are known which will enable the reaction to take place at any required temperature, the astounding flexibility of this part of the process from a commercial standpoint is immediately apparent.

In this process especially the economics have to be carefully calculated of the percentage of feed-oil to be converted per passage, since upon this the production of petrol from a given volume of catalyst in unit time, the size of distillation units, and other auxiliaries depend.

The yields obtained by this process vary according to the temperature of the reaction and the products required from : 80-93 per cent. of petrol ; 5 per cent. of water ; and 20-7 per cent. of gas, with a hydrogen absorption of 4·5-6 per cent. by weight.

All the equipment except that used in the actual hydrogenation reactions is equipment standard either to the synthetic ammonia industry or the petroleum industry. Hydrogen can be conveniently made from the hydrocarbon gases by reaction with steam over a catalyst, but as research improves the yield of petrol and decreases the yield of these gases, the installation of plant for the production of hydrogen by some other method becomes necessary. This is a subject which has been thoroughly explored by the ammonia industry. The method used will vary with the sites chosen for the hydrogenation plant.

The other equipment required, for debutanisation, petrol recovery, stabilisation, and petrol refining, is so much an integral part of normal petroleum production that no description is required here. It should be mentioned, however, that hydrogenation petrol requires little refining. Removal of dissolved hydrogen sulphide, removal of a trace of phenols in the petrol produced directly from coal, but not in that from the vapour phase, and little more, is required. If the vapour-phase petrol is an aromatic one, a wash with strong sulphuric acid is required since there is a tendency to form gum with this petrol, but the naphthenic petrol is completely stable.

	(1)	(2)	(3)
Sp. gr. 15/15° C. . .	0·755	0·751	0·7425
I.B.P. °C. . . .	49	33	44
10 per cent. °C. . .	74	81	65
30 ,, ,, . .	93	100	88·5
50 ,, ,, . .	108	116	108
70 ,, ,, . .	126	133	129
90 ,, ,, . .	152	155	159
F.B.P.	175·5	168·5	181
per cent. at 100° C. .	43	30	42
Colour	Bright water white	Bright water white	Bright water white
Acidity . . .	nil	nil	nil
Corrosion test (copper dish). . . .	negative	negative	negative
Elemental sulphur .	,,	,,	,,
Mercaptans . . .	,,	,,	,,
Total sulphur (per cent. by weight) . .	0·02	0·03	0·027
Gum content (mgrs./100 mls.):			
Pyrex dish . .	nil	0·7	0·1
Copper dish . .	0·02	0·04	0·4
Knock ratings, C.F.R. engine . . .	81	66	69

Petrol Quality.

Properties of typical petrols are given in the table on p. 19.

(1) is the petrol produced by the direct hydrogenation of the coal;

(2) is a naphthenic petrol produced by vapour-phase hydrogenation of middle oil; and

(3) is a blend produced by a complete plant, run under the conditions necessary to produce a No. 1 petrol.

The arrangement of both semi-technical and commercial plants is such that the light ends of the petrol from any stage are carried forward from the separators by the stream of circulating gas and recovered separately. It is for this reason that the volatility of the petrols (1) and (2) is low, since these light ends are not blended into their appropriate petrols, but are added only to the final blend to give it its necessary distillation curve.

As stated before, the variations possible in the method of running the vapour-phase plant give us complete control over the volatility, the 70 per cent. distillation point, and the knock rating, and any variations in specification that can be met by crude petroleums can be met by coal hydrogenation spirits.

Other Oils.

By the choice of appropriate conditions, fuel oil, Diesel oil, safety fuel, aviation spirits, kerosene and white spirits, etc., have been produced. As has been stated earlier, the first stage of the hydrogenation of the coal can be controlled so that primarily heavy oil is produced. The distillate heavy oil makes an excellent fuel oil and a typical oil will have properties similar to the following :—

Carbon	90·12 per cent.
Hydrogen	8·43 ,,
Nitrogen	1·11 ,,
Sulphur	0·17 ,,
Ash	0·022 ,,
Hard asphalt	0·98 ,,
Calorific value	9736 cals./gm.
Viscosity at °C. (Admiralty)	785 sec.
Flash point (Pensky-Martin)	280° F.

Since the original coal molecules are probably of an aromatic structure, it is certainly easier to produce aromatic oils than paraffinic oils. A true paraffinic Diesel oil has not yet been produced by the hydrogenation of coal, but there is no difficulty in producing a good paraffinic-naphthenic Diesel oil in place of a proportion of the normal petrol production. A summary of the properties of such an oil is :—

Sp. gr. 15/15	0·8360
Flash point	178° F. (81·2° C.)
I.P.T.:	
I.B.P.	217·5° C.
10 per cent at	222·5° C.
30 „ „	227·0° C.
60 „ „	236·0° C.
90 „ „	257·0° C.
F.B.P.	283·0° C.
Total distillate	98·5 per cent.
Residue	1·5 „
Ash	0·002 „
Asphalt	nil
Setting point	below — 50° F.

Total *acidity* equivalent to 13·5 mgm. KOH/100 gm. oil. Inorganic alkalinity equivalent to 1·2 mgm. H_2SO_4/100 gm. oil.

Viscosity:	
32° F. Admiralty viscometer	5·0 secs.
70° F. Redwood No. 1	33·5 „
140° F. „ „	28·3 „
Carbon	85·94 per cent.
Hydrogen	13·46 „
Sulphur	0·08 „
Calorific value	10,987 cal./gm.
Moore spontaneous ignition temperature	265° C.

Hydrogenation of Crude Oil.

The first large-scale plant for the hydrogenation of crude oil was erected in 1929 at Bayway, New Jersey, U.S.A., by the Standard Oil Company of that State, in co-operation with the I.G. Farbenindustrie (*Ind. Eng. Chem.*, 1930, **22**, 1030). Hydrogen for the process is made by heating hydrocarbons with steam. The pressure employed is about 200 atms., and the temperature from 400-500° C. The following are stated to be the five principal adaptations of hydrogenation as far as the oil industry is concerned :—

(1) Conversion of heavy high sulphur asphaltic crude oils and refining residues into gasoline.

(2) The alteration of low-grade lubricating distillates to obtain high yields of lubricating oils of premium quality.

(3) Conversion of inferior burning oil distillates and light gas oils into high gravity low sulphur water-white oil of excellent burning characteristics.

(4) The desulphuration and colour and gum stabilisation of high sulphur, badly gumming, cracked naphthas without marked alteration of distillation range.

(5) Conversion of paraffinic gas oils into low sulphur gum and colour stable good anti-knock gasoline.

In May, 1933, the hydrogenation of crude oil fractions to produce lubricating oils had become an accomplished commercial process, and such oils are now marketed in Great Britain by the Anglo-American Oil Co. Ltd., under the descriptive name of "Essolube," at prices no higher than ordinary lubricants.

Two interesting papers on the hydrogenation of crude oil by Haslam and collaborators were given recently before the World Petroleum Congress (July, 1933). The first of these dealt with a comparison of cracking and hydrogenation for gasoline production, and may be briefly summarised as follows :—

In the high-temperature operation—as demonstrated in the commercial units of the I.G. Farbenindustrie, A.G., and the pilot plant of the Standard Oil Company of Louisiana—hydrogenation intensity is so limited that non-paraffinic gasoline is produced, but without the formation of tar or coke. The resulting gasolines are low in sulphur, are gum stable and require only minimum amounts of treating. High-flash high-octane number safety fuel and high-solvency paint and lacquer naphthas are among the products made in this operation. The comparative results are given from three catalysts in the production of gasoline at high temperature from the same gas oil at periods of equal catalyst age. These show that the more active catalysts are primarily effective in increasing throughputs and conversions. The gasoline production per unit volume of catalyst has been more than doubled, and such results are of considerable economic importance since they make possible more efficient utilisation of high-pressure reaction equipment.

With low-temperature operation the outstanding characteristics of a highly active catalyst recently demonstrated by the I.G. Farbenindustrie are : (*a*) High yields—on the average up to 110 gallons of gasoline from every 100 gallons of gas oil ; (*b*) high conversion per pass—usually 50-100 per cent. better than that possible on catalysts previously used ; and (*c*) the gasoline produced is of high volatility (40-45 per cent. off at 212° F.) and requires no finishing treatment other than a caustic or soda wash, followed by a light doctor sweetening. A table is given showing details of production and properties of gasolines produced in this way.

From comparative details given of operating conditions and products made from five stocks by (*a*) cracking, (*b*) high-temperature hydrogenation, and (*c*) low-temperature hydrogenation, the authors conclude that—

(1) Both hydrogenation methods offer substantial increases in gasoline yields over cracking in all cases. Whereas cracking produces 90-95 volumes of liquid product (per 100 volumes of feed), of which usually 50-75 volumes are gasolines and the rest tar, hydrogenation yields 90-110 volumes of gasoline on the same basis.

(2) Higher conversions are realised with hydrogenation.

(3) Since only a caustic wash is required on the low-temperature hydro gasolines, negligible treating losses and losses of octane rating are encountered on these products.

(4) The octane numbers (Series 30 motor at 212° F. jacket temperature) of the cracked gasolines are in general higher than those presented for the hydrogenated products. This apparent advantage, however, is counterbalanced in large measure by the superior lead susceptibility and " non-fading " properties of the hydrogenated fuels.

The authors then discuss in detail the bases of comparison used in their calculations, comprising (*a*) hydrogenation plant, (*b*) cracking unit, (*c*) octane number credits, and (*d*) by-product credits. Following a survey of the influence of price structure and of changes in low-temperature hydro gasoline volatility on the economic position of the hydrogenation process, the authors finally arrive at the following conclusions :—

(1) The economic position of the hydrogenation process is markedly affected by gasoline price. At low gasoline prices hydrogenation offers no, or only small, advantages over cracking. High gasoline prices are favourable to the hydrogenation process.

(2) The low-temperature hydrogenation process appears more advantageous than the high-temperature process. It offers attractive returns on the additional hydro investment at a gasoline price of 6 cents/gallon and above.

(3) Low aniline point, high-boiling range gas oils and cycle stocks are the most attractive charging stocks for hydrogenation.

(4) In refinery situations where the high volatility of the low-temperature hydro gasolines cannot be utilised by blending off with naphthas deficient in light ends, some reduction in yield must be taken. This correction decreases somewhat the returns possible on the additional investment, although the low-temperature hydro process still looks attractive at gasoline market prices of 6 cents/gallon and above.

In evaluating the hydrogenation process its adaptability to a wide range of stocks and its convertibility to other operations, such as lubricating oil improvement, water white production and hydrofining of cracked naphthas, should be considered. Moreover, the hydro process manufactures a given quantity of gasoline from a smaller amount of feed stock than cracking. In a plant long on fuel oil, gasoline requirements can be met by processing a smaller amount of crude oil, when using hydrogenation, with an accompanying reduction in fuel oil. For example, the introduction of one low-temperature hydro unit in a typical refinery under study will reduce the crude oil requirements 14 per cent. and drop the ratio of fuel oil to gasoline from 2·4 to 1·9.

The low-temperature hydrogenation process gives gasoline yields of high A.P.I. gravity and high volatility (40-50 per cent. at 212° F.). In some refinery situations the use of hydrogenation would obviate casinghead purchases. Furthermore, this method of operation, since the gasoline produced requires only a soda or caustic wash, decreases or eliminates treating equipment, rerunning equipment and acid recovery plant.

The second paper by Haslam and collaborators is in connection with the properties of hydrogenated motor lubricating oils, and the following abstract deals with the main features of the paper :—

The present-day trend in automotive design, toward increase of compression ratio, higher speeds and greater bearing loads, results in severe operating conditions which can be met satisfactorily only by the best of lubricants. Experience gained during the past three years in laboratory and field tests has shown that hydrogenated motor oils, in addition to meeting the exacting requirements of automotive lubrication adequately, have actually demonstrated superior performance to even the best natural lubricants.

Since the operating viscosity of a lubricant is fixed by engine design, operating conditions and atmospheric temperature, the properties which are desired in a superior lubricating oil are : (*a*) High viscosity index ; (*b*) low consumption ; (*c*) minimum tendency to form carbon and sludge ; (*d*) high lubricating value or oiliness ; and (*e*) rapid distribution to bearings.

Oils of high viscosity index (good viscosity-temperature relationship) have relatively low viscosity at low temperatures and relatively high viscosity at high temperatures. The former is important in starting engines in cold weather. Since engine cranking speed has been found to be the controlling factor in cold starting, low viscosities at low temperatures are imperative. Oils of high viscosity at low temperature lower the cranking speed of the engine, retarding or preventing its start. At high temperatures, such as those encountered on engine cylinder walls, the high viscosity index oil does not thin out excessively and lose its " body." High viscosity under hot-engine conditions ensures perfect lubrication and the maintenance of a good piston seal.

The effect of viscosity index on the low and high temperature viscosities of oils, all having the same viscosity at 210° F. (60 Saybolt seconds), is clearly shown by the table on opposite page.

At zero degrees Fahrenheit (with oils of equal viscosity at 210° F.), oils of 100 viscosity index have only one-sixteenth the viscosity of oils of zero viscosity index, yet at 400° F. they have 26 per cent. higher absolute viscosity than the zero viscosity index oils. For maximum economy in operation it is imperative that motor lubricants have a low rate of consumption and require infrequent changing.

Viscosity Index.	0.	50.	100.
Redwood seconds at 0° F.	625,000	196,000	38,300
,, ,, 200° F.	58·4	58·0	57·5
,, ,, 400° F.	28·2	29·5	30·1
Kinematic viscosity at 400° F. (Centistokes)	1·52	1·64	1·92

A superior lubricant must have a minimum tendency to deposit carbon and form sludge. Carbon accumulated in the combustion space causes pre-ignition and increases detonation, with resultant loss of power. In extreme cases it prevents freedom of valve action, with eventual burning and pitting of valves.

A related phase of carbon formation frequently encountered is piston ring sticking. The carbonaceous mass which often develops, due to lubricants coking and oxidising in the piston ring slots, causes the rings to stick. As a result piston seal is lost, causing loss of power, high oil consumption and in extreme cases scored cylinders or burned-out pistons. Excessive " blow-by " occurs also, permitting obnoxious odours to escape from the crankcase into the interior of the car.

Although the exact mechanism of sludge formation is not completely understood, it appears to be caused by the combined influence of the products of oxidation of the oil and the condensation of the water vapour in the " blow-by " gases (gases leaking by piston ring) entering the crankcase. Analyses of typical sludges are :—

Type.	Crankcase Sludge, per cent.	Valve Chamber or " Mayonnaise " Sludge, per cent.
Naphtha soluble (oil)	57·0	62·5
Chloroform soluble (asphaltic material)	15·6	—
Water	1·0	28·0
Residue—		
Carbonaceous material	16·7	7·5
Ash *	1·6	0·5
Oxygen, sulphur, nitrogen, etc.	8·1	1·5
	100·0	100·0

The " crankcase " type sludge frequently causes plugging of oil screens and oil lines with resulting failure in lubrication. The

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* Consists largely of Babbitt particles with some iron.

" mayonnaise " type is often found in poorly ventilated valve compartments, particularly on overhead valve engines with worn exhaust-valve guides which permit leakage of exhaust gases into the valve chambers.

High lubrication value, frequently referred to as " oiliness," has become of increasing moment with the advance in engine design during the past few years. High compression ratios, with attendant higher mean effective pressures, and the higher bearing loads due to increased speeds, demand oils of maximum lubricating power.

In addition to these properties, the modern lubricant must have good " pumpability " at low temperatures. In other words, it must flow readily to the oil pump when the motor is started in cold weather and must be distributed immediately and uniformly to bearings. High viscosity index oils with low pour points have been found to satisfy these requirements most effectively.

Of the natural lubricants available, paraffinic-base oils come nearest fulfilling the requirements outlined above. Since they possess high viscosity indices, they permit easy starting. Their high viscosity at high engine temperatures is desirable. They resist oxidation and hence do not sludge excessively. They are not consumed rapidly. They do form, however, large quantities of hard scaly carbon. Moreover, being difficult to dewax, they often have high pour points. Naphthenic-base oils have the advantage of low pour point and small porous lamp-black type carbon formation. They have, however, very poor viscosity indices, poor oxidation resistance and high consumptions. High viscosity index oils have the advantage of high molecular weight, high boiling-points and high A.P.I.* gravity (low specific gravity).

Properties of Hydrogenated Oils.

The process for hydrogenation of lubricating oils, as carried out commercially by the Standard Oil Company (N.J.), is particularly effective in removal of impurities. During hydrogenation, oxygen, nitrogen and sulphur are practically eliminated and asphaltic and carbonaceous material converted to stable hydrocarbons or removed. In addition to the hydrogenation of unsaturated compounds and aromatics, there is some tendency to split open and further hydrogenate ring- or naphthenic-type compounds.

The net result of these reactions is to produce an oil which is of higher hydrogen content and therefore more paraffinic than the original starting material. The hydrogenated lubricants may have viscosity indices equal to the best natural lube oils. Hydrogenated oils are further characterised by their high flash, excellent colour, high A.P.I. gravity and low Conradson carbon content.

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* Gravity scale adopted by the American Petroleum Institute.

Operating Characteristics.

As outlined above, lubricants of high viscosity index give the most satisfactory cold-starting performance. Low viscosity at low temperature is important since the torque required during cranking is a function of the viscosity of the oil at the temperature of cranking. Hydrogenated oils, by virtue of their high viscosity index and therefore low viscosity at low temperature, permit the engine to attain high cranking speeds, thus ensuring a quick and easy start. Tests made on a number of engines have demonstrated that hydrogenated motor oils have cranking properties practically equal to the best Pennsylvania lubricants. The following table presents cranking results obtained on a Chrysler motor at 0° F., using oils of the same viscosity at 210° F. :—

	Pounds/feet.
Hydrogenated motor oil, 0° F. pour point	345
Pennsylvania oil 0° F. pour point	343
Typical " mixed base "	475
Typical coastal oil	850
Highly refined coastal oil	1,750

While ease of starting is determined by oil viscosity, the pumpability of an oil is controlled principally by its pour point and viscosity index. Hydrogenated lubricants, treated with paraflow, have shown excellent low-temperature pumping characteristics and absence of any tendency to channel. These properties ensure immediate flow of oil to the pump and rapid and uniform distribution to the bearings of the engine when starting in cold weather.

Before discussing the specific consumption characteristics of hydrogenated motor oils, it may be well to emphasise the effect of speed on oil consumption. Tests made at the Indianapolis Speedway in 1931, at General Motors Proving Grounds at the Fuel and Lubrication Laboratories of the Standard Oil Development Company, and at other laboratories, have proved conclusively that oil consumption may be seven to twenty times as much at high speeds as at moderate speeds. Information obtained in two eight-cylinder cars at the Fuel and Lubrication Laboratories of the Standard Oil Development Company shows that both cars consumed about nine times as much oil at 60 miles per hour as at 30 miles per hour.

This increase in consumption at high speed may be accounted for largely by " pumping." The piston rings when moving so rapidly at high motor speeds apparently fail to scrape off the excess oil supplied to the walls. This oil is pushed or " pumped " by the rings into the combustion chamber where a part of it is burned and expelled with the exhaust gases. This condition is aggravated by stuck piston rings. Leakage through crankcase and bearing joints, which increases with the decrease in oil viscosity at the high oil temperatures developed during high-speed driving, is responsible for some of the increased consumption at high speed.

However, hydrogenated lubricants have demonstrated lower consumptions than even the best natural lubricants on a large number of cars and trucks under varying conditions of service. Typical laboratory test data obtained on a 1932 Packard follow :—

Speed, miles/hour	37·5	45	60
Consumption, miles/quart :			
Hydrogenated lube oil, S.A.E. * 40	3500	960	127
Pennsylvania motor oil S.A.E. * 40 . .	2000	400	106

At high speed the hydrogenated motor oil showed a 20 per cent. increase in oil mileage over the Pennsylvania oil, while at moderate speed the advantage was even more marked. Actual road tests, each of 2500 miles duration, on a 1932 Buick Sedan car have shown the following, which indicates a marked advantage for the hydrogenated lubricant :—

	Hydrogenated Motor Oil.	Pennsylvania Motor Oil.
Inspection of oils :		
Saybolt viscosity at 210° F.	63·2	61·4
Redwood viscosity at 200° F.	59·8	58·0
Kinematic viscosity at 400° F. in Centistokes .	1·96	2·0
Viscosity index	90	103
Conradson carbon, per cent.	0·26	0·519
Flash, °F.	450	435
Oil consumption, miles/quart	560	420

It has been recognised for some time that the flash point of a motor oil plays an important rôle in oil consumption. It has been pictured that the light constituents of a low-flash oil vaporise at the temperatures obtaining in the engine and leave the motor with the exhaust gases or go out through the crankcase breather. Substantiation of this theory has been obtained by studying the change in properties of oils during motor tests. Coastal oils, typical examples of low-flash oils, have high consumption and give an increase in flash and viscosity of the oil left in the crankcase after operation (crankcase dilution removed from used oils before making inspection). For instance, in a 48-hour test on a Ford motor, the flash of a Coastal oil increased from 325° F. on the original oil to 360° F. on the used crankcase oil, indicating considerable evaporation.

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* Viscosity scale adopted by the Society of Automotive Engineers.

On the other hand, information assembled during the past few years on hydrogenated oils have pointed to the conclusion that other factors, particularly viscosity index, may be even more important than flash in determining oil consumption. The following table presents consumption data taken on a 1930 Packard when running on a hydrogenated oil, a " specially refined " hydrogenated oil and a Pennsylvania oil :—

Oil.	Hydrogenated Lube.	Special hydro-Lube.*	Pennsylvania Lube.
Viscosity index	87	108	99
Saybolt vis. at 210° F.	73·6	70·9	71·8
Redwood vis. at 200° F.	71·8	69·6	70·0
Redwood vis. at 400° F.	30·5	31·0	30·8
Kinematic vis. at 400° F. in Centistokes	2·20	2·33	2·24
Flash, °F.	475	440	460
Fire, °F.	555	510	525
Conradson carbon, per cent.	0·279	0·052	0·796
Consumption data, miles/quart :			
At 45 miles/hour	950	1110	392
At 52½ miles/hour	256	228	151
At 60 miles/hour	127	115	105

Although having a flash point 20° F. lower than the Pennsylvania oil, the " specially refined " hydrogenated oil was consumed at a lower rate than the Pennsylvania oil at all speeds. At 45 miles per hour the " specially refined " hydrogenated oil showed superior performance to even the hydrogenated oil, although the flash of the latter was 35° F. above that of the former.

These tests indicate that the lower flash of " specially refined " hydrogenated oil was compensated for by its high viscosity index, and hence high viscosity at high temperature. It would seem plausible that, providing an oil has a flash point above some minimum value, flash point has only a limited effect on oil consumption. Based on the data in the last table, two tentative conclusions can be drawn at present :—

(1) The performance of the " specially refined " hydrogenated oil indicates that viscosity index may be more important than flash (provided the flash is above some minimum value) in determining oil consumption.

(2) The superior consumption characteristics of the hydrogenated oils over the Pennsylvania oil may be interpreted on the basis that the former have a more stable structure, resisting oxidation and

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* Specially treated to extra high viscosity index.

decomposition better under the severe conditions obtaining in the cylinders of an engine running at high speed.

Experience with hydrogenated lubricants has been equally gratifying in bus and motor-truck service as with passenger cars. Laboratory test data on motor-truck engines has already been described by Haslam and Bauer. A 25 per cent. increase in oil mileage has resulted from the use of hydrogenated motor oils in a fleet of 41 White Heavy Duty buses operating in the vicinity of New York. A study of some 30 trucks and buses operating with hydrogenated oil in regular city service in the United States has shown an improvement in oil consumption in practically all cases. Based on information available to date, a test on a number of A.E.C. buses in London has shown about 30 per cent. increase in oil mileage when using hydrogenated oils instead of the high-grade Mid-Continent oil previously employed.

Hydrogenated motor oils, by virtue of their high degree of chemical purity, form only minimum amounts of carbon and sludge. Carbon deposition may occur in three distinct forms in the automotive engine : the sooty type which is usually blown out in exhaust gases, the coarse granular type which wedges between piston rings and walls causing wear due to its abrasive nature, and the scaly, curly type which tends to build up the combustion space. This latter is especially detrimental since its fine edges and sharp points become incandescent due to the heat in the combustion chamber, and cause pre-ignition and detonation. Hence, as carbon accumulates in a motor, other factors being equal, the tendency to knock will become more pronounced. This tendency is accentuated with oils forming large amounts of carbon. To investigate this point 2500-mile runs were made on a hydrogenated motor oil and a Pennsylvania oil with a 1932 Buick Sedan. The car covered a prescribed course each day. Knock tests were carried out on a hill of uniform grade. Some 18 knock determinations were made daily. The car was accelerated up this hill, under full throttle, the speed at which disappearance of the knock occurred being observed. The results of these tests show that both oils had a similar and steady increase in the minimum speed for knock disappearance up to about 1600 miles. Beyond this point the Pennsylvania oil gave decidedly inferior performance while the hydrogenated oil tended to approach equilibrium. At the end of the test, 2600 miles, knock disappearance was observed with the hydrogenated oil at a speed 10 miles per hour less than with the Pennsylvania oil.

The experience of a large company operating many White Heavy Duty De-luxe buses may be of interest in this connection. These buses operated normally 200 miles per day each over hilly routes and through New York City traffic. The results are as follows :—

(1) Prior to the use of hydrogenated motor oils in these buses, considerable trouble was encountered with carbonising around piston rings. The use of hydrogenated lube has reduced this practically to zero. It has been demonstrated that it is now possible to run the engines over 100,000 miles without removing pistons. After a piston had been in operation continuously for 119,395 miles, a photograph shows that only a thin film of carbon has built up on the head of the piston, the rings are free, with only negligible amounts of carbon deposited behind them, and the piston rings show absence of scoring or scratches.

(2) Carbon does not accumulate rapidly, and is now removed only at the routine 50,000 miles check-up on valves, bearings, etc.

(3) Troubles previously encountered on valve chamber and crankcase sludge have been reduced to zero by the use of hydrogenated motor oils.

(4) Since using the hydrogenated oils, no bearing failures due to faulty lubrication have been observed.

(5) No exhaust valve sticking has been observed with the hydrogenated oils.

(6) The use of hydrogenated oil has resulted in an increase of over 25 per cent. in oil mileage.

Another example of the performance of hydrogenated oils is as follows : A careful investigation of another fleet of trucks and buses operating on regular city service has been made. Engines used on the buses in question include Hercules, G.M.C., Ford, A.C.F. White and Studebaker. A total of 200,000 vehicle miles was completed during the test period. The tests permitted the following conclusions :—

(1) The hydrogenated oils gave markedly better oil consumption in practically all cases.

(2) The hydrogenated oils showed no evidence of sludge formation, although appreciable quantities had resulted during use with the previous oils.

(3) In some cases the hydrogenated oil tended to loosen flaky carbon from pistons and connecting rods during the first 100 miles. This scouring action was confined to this period; the amount of carbon collected during the subsequent 3000 mile test was very small.

(4) Difficulties with sticking piston rings and carbonised exhaust valve ports were reduced.

(5) In a number of cases increased gasoline mileage was also observed, due very probably to the maintenance of better piston seal and cleanliness around the piston ring area with the hydrogenated oil.

Investigations have recently been conducted at service stations in seven cities along the Atlantic seaboard over a 30-day period with a new apparatus for determining sludge in crankcase oils. This device consists essentially of a standard light, a sensitive photronic cell and an indicating ammeter. A beam of light is directed through a thin film of the crankcase drainings on to the cell, which registers the amount of light not absorbed by the oil. Used oils containing large amounts of suspended sludge allow only small amounts of light to get through to the cell. The indicator is so calibrated that it classifies the oils as good or fair and bad. The test results, which include only those cases where the mileage since previous drainage is definitely known, are summarised in the following table :—

Miles run without changing	0-500		500-1000		1000-5000	
Kinds of oil	Competitive	Hydrolubes	Competitive	Hydrolubes	Competitive	Hydrolubes
Number of cars	130	173	280	488	131	367
Percentage in good or fair condition	40·0	80·9	33·2	60	16·8	28·1

These tests show a decided improvement of the crankcase oil condition for cars using hydrogenated oil. As would be expected, there is a steady decrease in the cleanliness of crankcase oils studied as the mileage increases. However, even in the 1000-5000 mile range, the hydrogenated oil shows a marked superiority.

During the past decade the trend in automobile design has been toward higher compression ratios, higher speeds and increased power. Advances of 22 per cent. in speed and 50 per cent. in power have been made without increase in engine size. This tendency has been given particular impetus in England and on the Continent, where automobile taxes are usually based on cylinder volume. Cars with compression ratios of 7·1/1 and speeds of 4000 r.p.m. are not uncommon in Europe to-day. These changes have produced more exacting operating conditions for the modern motor oil—in addition to having high viscosity at high temperature and minimum tendency to deposit carbon, it must be able to withstand high bearing loads at high speeds. In other words, it must have high " lubrication value " or " oiliness."

A machine has been designed by the Fuel and Lubrication Laboratories of the Standard Oil Development Company to study bearing failures at high speed and to determine the variations with different type lubricants. The machine consists essentially of a connecting-rod bearing which can be loaded in increments of 500 lbs. by means of a spring at varying speeds. Oil is supplied to the bearing at 20 lbs./sq. in. gauge. The test procedure is to increase the bearing load up to 3800 lbs., which corresponds to 760 lbs./sq. in. bearing pressure, at a constant speed of 3000 r.p.m. After this load is reached the speed is increased by increments of 200 r.p.m. until failure occurs. Comparative tests made on a hydrogenated oil, a Pennsylvania oil and a castor-oil blend with this machine are reported as follows :—

Oil Tested.	Hydrolube.	Pennsylvania Oil.	Castor-oil Blend.
Saybolt viscosity at 210° F.	85·2	83·5	80·4
Redwood viscosity at 200° F.	84·5	82·5	80·1
Viscosity index	92	96	82
Flash, °F.	500	475	340
Conditions under which failure occurred :			
Bearing pressure, lbs./sq. in.	760	760	760
Speed, r.p.m.	4000	3600	3200
Bearing temperature, °F.	293	311	311
Torque, inch-pounds (friction preceding failure)	6·3	8·5	9·3

Although the test programme on this machine is not sufficiently complete to permit drawing final conclusions as yet, Haslam states that the work indicates that hydrogenated motor oils have lubricating properties equal to or better than castor-oil blends, for this type of high-speed lubrication, carrying a load whose position on the bearing is constantly shifting. It has also been observed on this machine that if the oil supply is momentarily cut off at these high speeds, bearing failure occurs almost instantaneously. This further emphasises the necessity for oils forming minimum amounts of sludge. The clogging of oil lines or plugging of the oil-pump screen by sludge can readily lead to bearing failure.

Apart from hydrogenation, pressure is being increasingly employed in the petroleum industry in the cracking of heavy petroleum oils to produce gasoline fractions. The average temperature employed is 900° F., and the pressure 700-1500 lbs. per sq. in. A typical installation of this character is the " Cross " cracking plant installed on the Isle of Grain in the Thames Estuary (Rogers, *Trans. Inst. Chem. Eng.*, 1927, **5**, 89), which is described in detail in Chapter IX.

The principle of " cracking " is to convert a petroleum body of a given gravity into other hydrocarbon bodies, some of which are of less and others of greater gravity than the parent stock. At the end of the nineteenth century the light fractions of petroleum now known as petrol were unsaleable, and a definite drug on the market, but with the advent of the motor-car and lorry, and later the aeroplane, these light fractions became in such demand that the supply was inadequate. The subject of cracking thus gained an enormous impetus, and now a large proportion of our supplies of light petroleum are obtained in this manner.

These examples, taken from the great number now available, show the great importance of the rôle played by high-pressure processes in modern industrial chemistry. I have dealt with the subject of hydrogenation of coal and oil at considerable length because of recent important industrial developments in this respect. It is the purpose of this book to describe the principles of design based upon personal experience of high pressure extending over many years; in general the technique described will be more particularly applicable to the chemical engineering side of the subject, in the hope that it will prove of practical assistance to the increasing number of chemists and engineers engaged in this fascinating and fruitful field. It may be helpful from time to time to refer to the work of Bridgman and Poulter in America, Basset in Paris, Bone in England, and Michels in Amsterdam, who have done so much excellent work on the physical side of high pressures. The three former have reached pressures as high as 12,000-20,000 atms. as a routine pressure in their experimental investigations, and Bone has recently dealt with explosion pressures of the order of 10,000 atms.

Having spent some years as an engineer surveyor of steam and pressure plant before entering the high pressure field, I had excellent experience of the great importance of the safety factor in the design, operation and management of such equipment. The dangerous nature of operations at high pressure and temperature must never be overlooked by those responsible for the well-being of staff engaged on such work, and this introductory chapter is, therefore, not inappropriately concluded by reference to the regulations in respect of high-pressure plant at the Chemical Research Laboratory, Teddington.

These regulations include the following instructions :—

(1) The rate of pressure rise in vessels must not exceed a maximum figure, which is given for each vessel.

(2) The rate of temperature rise in high-pressure reaction vessels is also governed by definite instructions.

(3) No pressure joint, with the exception of gland nuts, must be adjusted under pressure.

(4) When dealing with carbon monoxide or other poisonous gas, two persons must always be present, and adequate ventilation ensured.

(5) In the case of oxygen or oxidising agent, oil or grease must be definitely excluded from the interior of the plant.

(6) A log book is kept for each plant unit, for the inclusion of all experimental data, and matters of interest such as repairs, tests, etc.

(7) The extent of individual responsibility is clearly defined.

CHAPTER II.

COMPRESSORS FOR HIGH-PRESSURE GAS COMPRESSION.

THIS section will be devoted to a discussion of actual designs of laboratory and large compressors, and high-pressure gas circulating pumps such as are used in high-pressure gas circulatory plants. It is not proposed to enter into any detailed discussion of the thermodynamics of the compressor cycle, as this would occupy a book in itself.

All machines for the compression of gas to high pressures are of the multi-stage type, with arrangements for efficiently cooling the compressed gas between each successive stage of compression. The reason for this will be illustrated in the following concrete example :—

It is desired to compress air to a pressure of 250 lbs. per sq. in. absolute. In the first instance, let it be assumed that compression is carried out in one cylinder, and that the compression is adiabatic. The temperature of the air after compression will be

$$T_2 = T_1(r)^{\frac{\gamma-1}{\gamma}},$$

where T_2 = Temperature of air after compression.

T_1 = Temperature of air before compression.

r = Ratio of compression $\left(= \frac{250}{14{\cdot}7}\right)$.

γ = Ratio of $\frac{\text{specific heat at constant pressure}}{\text{specific heat at constant volume}}$.

For air γ is usually assumed to be 1·4.

Taking the air temperature as 15° C. = 288° Abs.

$$T_2 = 288 \left(\frac{250}{14{\cdot}7}\right)^{\cdot 286}$$

whence $T_2 = 650°$ Abs. or 377° C.

At a delivery temperature of 377° C., it would be impossible to operate a compressor owing to difficulties with lubrication, valves, etc.

Now, instead of carrying out the compression in one cylinder, let the air be compressed in two stages, i.e. firstly to 60 lbs. per sq. in., in which case the temperature of the air leaving this compression stage would be of the order of 158° C. If this compressed air is cooled to a temperature of 15° C., before commencing the second stage of compression, the temperature of the air leaving the second stage of compression (pressure 250 lbs. per sq. in.) would be

$$T_2 = 288\left(\frac{250}{60}\right)^{\cdot 286}$$

whence $$T_2 = 433^\circ \text{ Abs. or } 160^\circ \text{ C.}$$

So that by stopping the compression process at an intermediate point, and cooling the air before proceeding with the second stage of compression, the final pressure of 250 lbs. per sq. in. has been attained with a delivery temperature of 160° C.

In practice, the compression is not quite adiabatic, but it is sufficiently near to serve as a fairly accurate illustration of the temperatures involved.

Considering the above example from the power point of view, when compressing the gas in one stage the work required per cubic foot of air at suction pressure (14·7 lbs. per sq. in.), can be found from the equation

$$W_E = \frac{\gamma}{\gamma - 1}P_1V_1\left\{\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right\}.$$

Substituting

$$3{\cdot}5(14{\cdot}7 \times 144)\left\{\left(\frac{250}{14{\cdot}7}\right)^{\cdot 286} - 1\right\}$$

$$= 9250 \text{ ft. lbs. per cu. ft. of aspired air.}$$

When the compression is carried out in two stages, the work done per cu. ft. of aspired air during the first portion of the cycle is

$$W_E = \frac{1{\cdot}4}{1{\cdot}4 - 1}(14{\cdot}7 \times 144)\left\{\left(\frac{60}{14{\cdot}7}\right)^{\cdot 286} - 1\right\}$$

$$= 3670 \text{ ft. lbs.}$$

In the second compression stage the work done per cu. ft. of air entering this stage at 60 lbs. pressure,

$$W_E = \frac{1{\cdot}4}{1{\cdot}4 - 1}(60 \times 144)\left\{\left(\frac{250}{60}\right)^{\cdot 286} - 1\right\}$$

$$= 15{,}100 \text{ ft. lbs.}$$

For this second portion of the process, we are beginning not with a cu. ft. of air at atmospheric pressure, but with the reduced volume which a cu. ft. of air will occupy when compressed to 60 lbs. per sq. in., so that the actual work required on the initial cu. ft. of air during the second compression stage is $15{,}100 \times \frac{14\cdot7}{60} = 3700$ ft. lb. Hence the total work required to compress 1 cu. ft. of air in two stages to 250 lbs. per sq. in. is $3670 + 3700 = 7370$ ft. lbs., compared with 9250 ft. lbs. for compression in one stage.

This smaller requirement of energy is explained by the smaller volume handled (by intercooling) in the second stage of the compression.

Another important aspect of multi-stage compression is that dealing with machine stresses. With single-stage compression, a certain piston area is necessary in order to deal with a certain initial volume of gas, and at the conclusion of compression the final pressure would be acting on this large area, thus causing very heavy cross-head and crank-pin loads. In addition, cylinders and covers would have to be designed on the basis of the final high pressure, and hence far stronger than necessary for the initial pressure of the gas. With stage compression, bearing loads and stresses can be well distributed and reduced very considerably.

Having shown the desirability of stage compression and intercooling, the remainder of the chapter will be devoted to a detailed description of various machines, each with its own characteristics and novelties in design.

Reavell Three-Stage Compressor.

Fig. 5 shows a photograph of a compressor by Reavell of Ipswich as recently supplied to the Cavendish Laboratory of Cambridge University. The constructional details are seen in Figs. 6 and 7. Two of these machines have been supplied to that laboratory, one for hydrogen and one for helium gas. When running at a speed of 600 r.p.m. the capacity of the machine is 18 cu. ft. of free gas per minute compressed to 200 atms.

The overall height of the machine is 5 ft. 2½ ins. ; it occupies a floor area of about 2 ft. square and the driving pulley flywheel is 2 ft. diameter × 3½ ins. wide for a 3-in. driving belt. The compressor is of the three-stage type, with two single acting first stages, and the second and third cylinders mounted above each of the two first stage cylinders. The machine may be said to comprise three essential parts :—

(1) A crank case in which the rotatory-reciprocating motion is fitted.
(2) The entablature which connects the crank case to the cylinders.
(3) The cylinders.

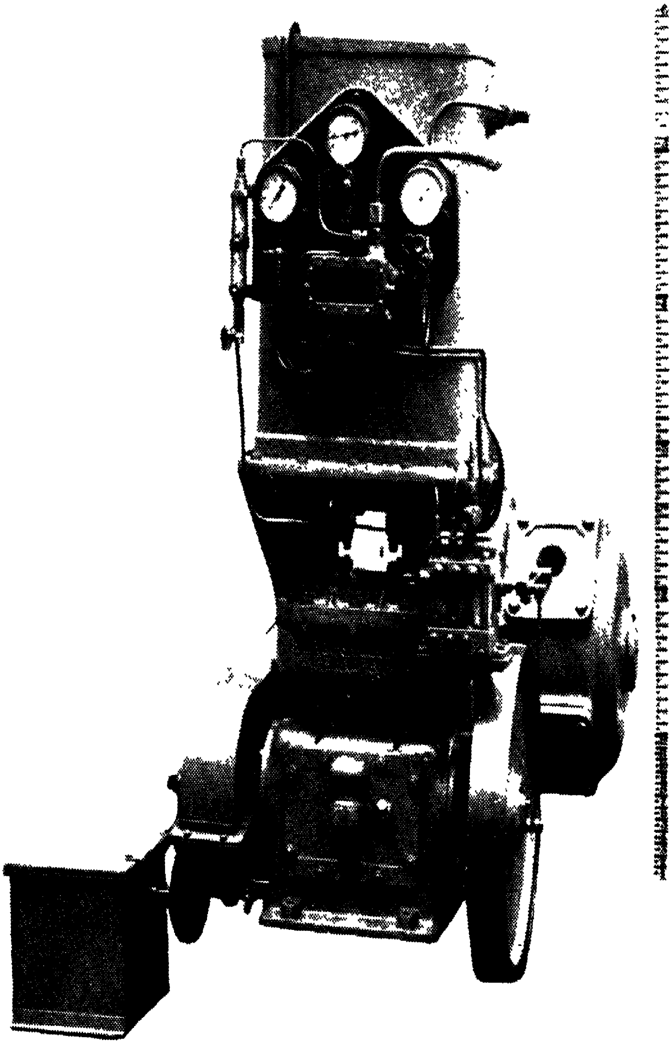


FIG. 5.—Reavell three-stage gas compressor.

[*To face page* 38.

Taking each of these parts in turn, the crank case is substantially built of cast iron and fitted with doors to allow of easy access to the working parts in the case. The two cross-head guides are of circular section, cast integral with the case and bored out to take the cross-heads. A large oil well is provided at the bottom of the crank case for lubricating oil. The crankshaft is of the two-throw type, with cranks set at 180°, and is made from Siemens-Martin acid open hearth forged steel. The connecting rods are also of this steel, with adjustable white metalled big ends, and bushed for gudgeon pins at the cross-head ends. The pins are of case-hardened and ground steel. The cross-heads are turned to a good fit in the circular trunk guides and the piston-rods are attached to these cross-heads by keys which are secured by nuts. These piston-rods are also of Siemens-Martin steel with ground finish.

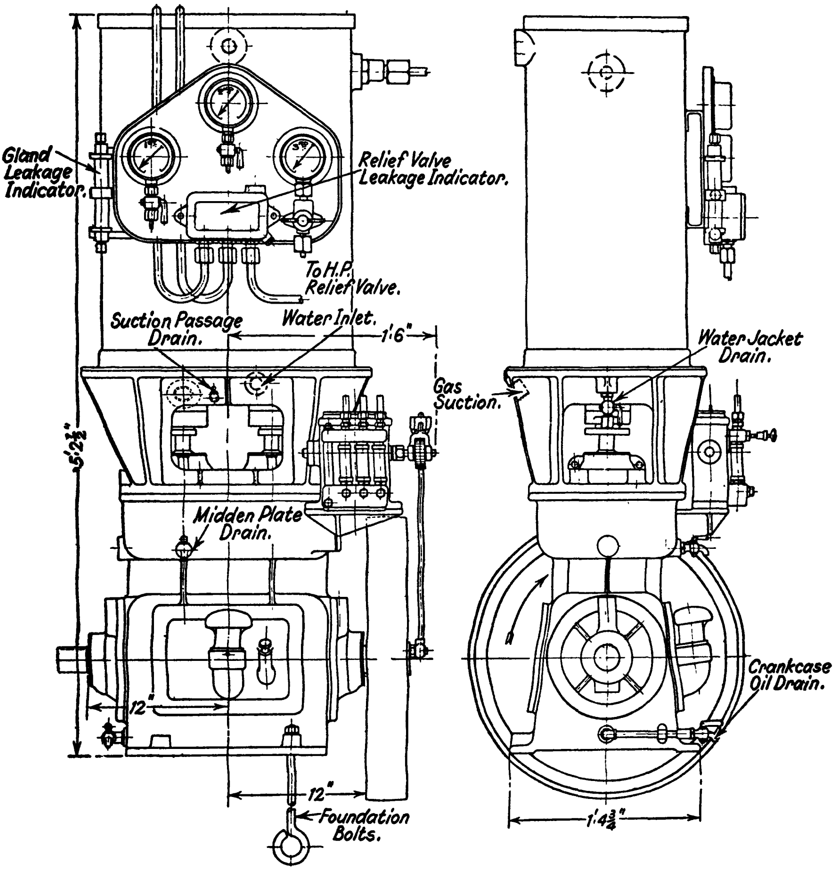


FIG. 6.—Reavell three-stage gas compressor.

The entablature serves as a base for the cylinders, and is provided with a flange to carry the water-cooling tank which surrounds the cylinders. In this entablature are formed the gland boxes for packing the first stage piston-rods, and in this gland box there is also a gas escape connection, so that the leakage can be returned to the suction side.

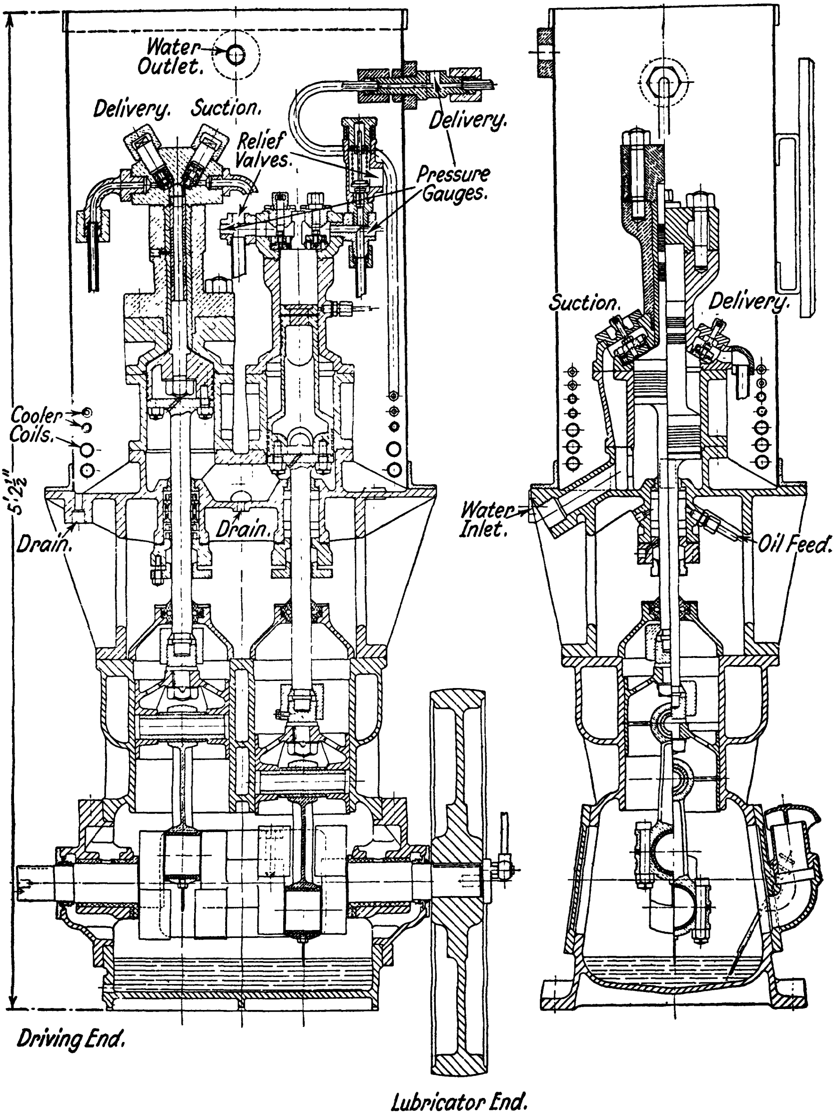


FIG. 7.—Reavell three-stage gas compressor.

The first and second stage cylinders are of best close-grained cast iron, and the third or final stage is a steel forging with a renewable cast-iron liner. The final stage cylinder cover is a steel forging, and the other covers are of cast iron. Metallic packing rings are fitted to all pistons. The first and second stage pistons are of cast iron with grooves turned in to take rings of the sprung-on type. The third stage piston is of the plunger type with cast-iron carrier rings and piston rings fitted alternately along its length.

The first and second stage cylinder valves are of the multiple ported low lift concentric ring type. The valves are made from thin discs of special steel, and the valve seats and guards from best quality close-grained cast iron. Each valve unit is assembled before insertion in the valve part of the cylinder into which it is rigidly held, as shown in Fig. 7, by means of a locking screw and nut. The third stage suction valve is of the mushroom type, and the delivery valve, which is of the thimble type, is made of high grade heat treated nickel steel and works on specially hard renewable seats. The compressed gas is cooled between each stage by passing it through coils of copper piping, and a similar procedure is adopted in cooling the gas from the delivery of the last stage before it finally leaves the machine. The coils are immersed along with the cylinders in a galvanised tank supported from the entablature.

A discussion of the method of preventing gas leakage from the piston-rods and past the high-pressure plunger piston has purposely been left until the last, as this is one of the most important points in any high-pressure compressor. The principle usually adopted is based upon the hydraulic seal obtained by fitting a small chamber of oil under pressure as high as, or slightly higher than, the gas pressure around the piston-rod, shaft or other moving part, whereby gas leakage is prevented by interposing this oil seal between the high-pressure gas and the atmosphere or gas at a lower pressure. This principle is so important in all high-pressure design that this will now be discussed in detail.

The idea is by no means new. James Watt conceived it in 1781, in connection with the double acting condensing steam engine, or that form of his single acting engine in which the top of the cylinder was open to the condenser on the up-stroke. In these circumstances there was always the risk of air leaking into the condenser, which, in reducing the vacuum, would seriously affect the performance of these early engines in which the steam pressure used was but little above that of the atmosphere.

The design of the lantern stuffing box as fitted by Boulton and Watt to the Wheal Towan engine in 1784 is shown in Fig. 8. (This is a copy of the actual working drawing made for this engine, and is reproduced from " James Watt and the Steam Engine," by Dickinson and Jenkins, by permission of the publishers, The Clarendon

Press, Oxford.) It will be seen that the cylinder cover is fitted with a sheet-metal dome, and the space thus enclosed is filled with steam by a steam pipe led direct from the boiler or main steam pipe. The steam fills the lantern and thus surrounds the piston-rod; condensed water is led away by pipe CC provided for that purpose.

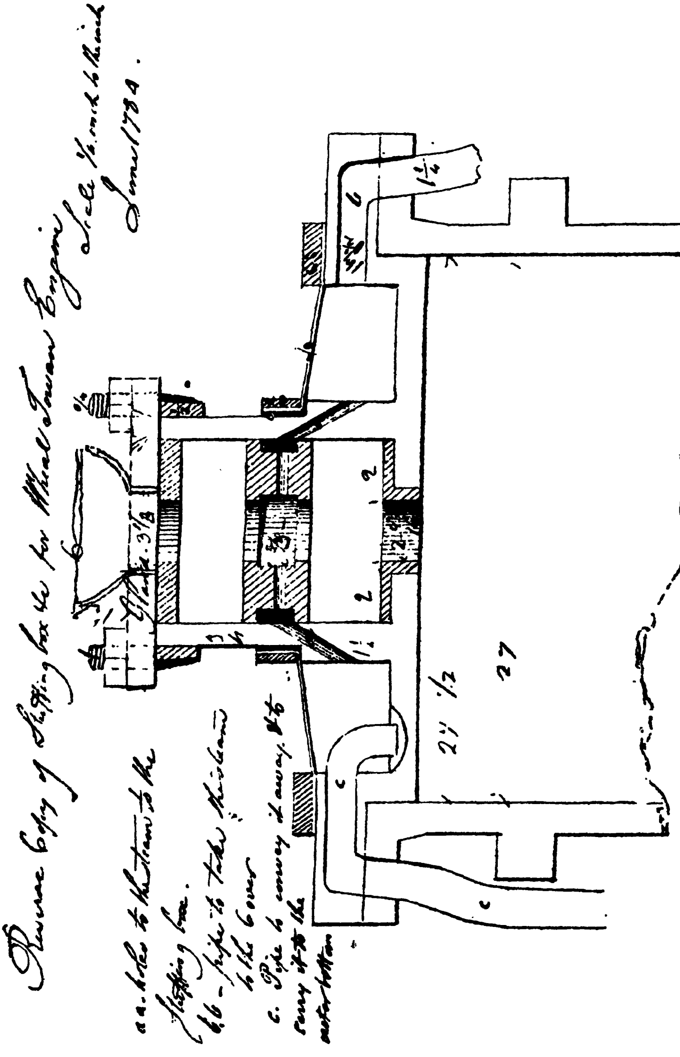

Reverse Copy of Stuffing box &c for Wheal Towan Engine
Scale 1/4 inch to the Inch
June 1784.
a. a. holes to the steam to the stuffing box.
b.b. - pipe to take the steam to the cover
c. Pipe to convey it away & to carry off the water bottom
3 3/8
2
1 1/4
24 1/2
27
c
c

FIG. 8.—Stuffing box for Wheal Towan engine, June, 1784.

Thus any leakage into the cylinder on the exhaust stroke will be steam and not air, and consequently the vacuum was easily maintained.

Throughout this chapter, it will be noted that all high-pressure compressor piston-rods are fitted with lantern ring stuffing boxes,

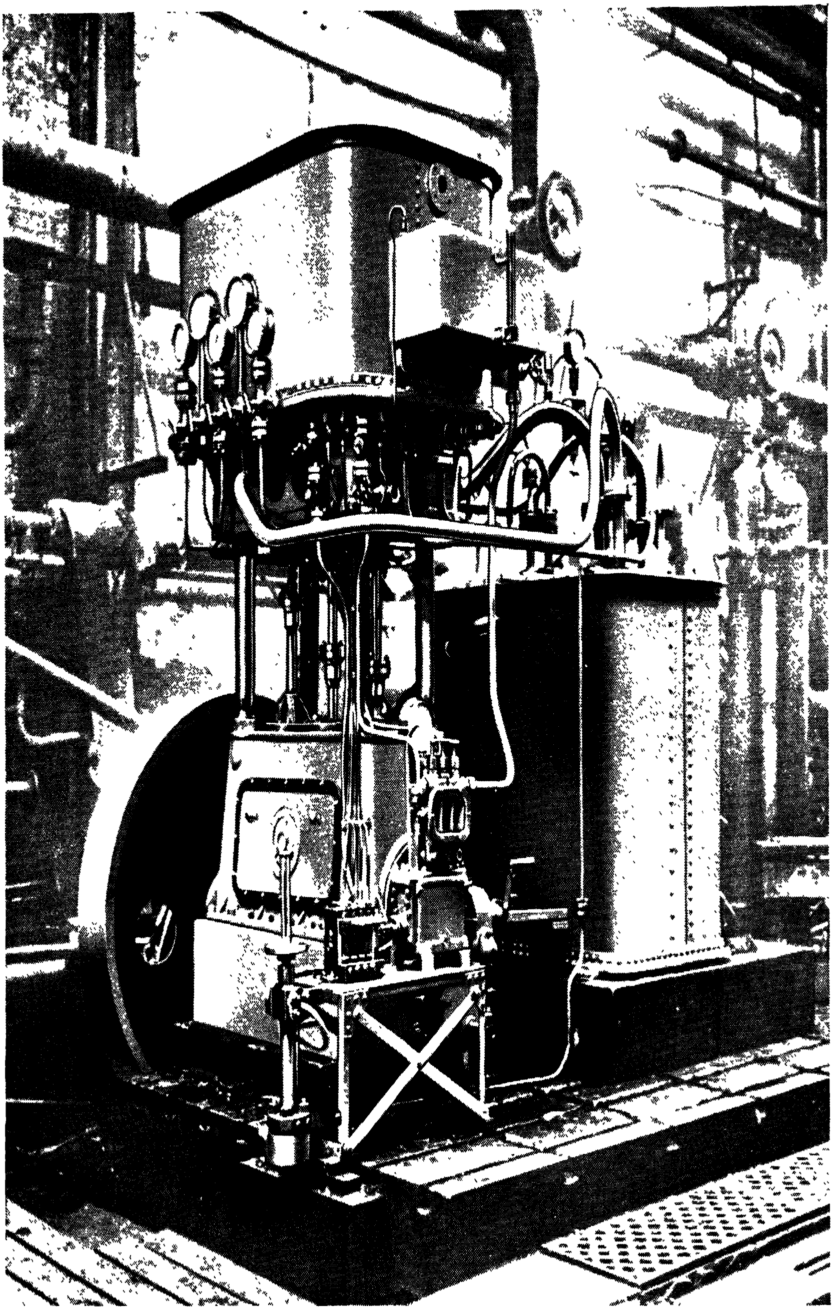


FIG. 9.—Brotherhood five-stage hydrogen compressor.

[*To face page* 43.

all based on the principle of the hydraulic seal. This principle is also adopted to seal the stirrer shafts of high-pressure autoclaves, and full details of this are given in Chapter VIII. When once the principle of this hydraulic seal in connection with the packing of stuffing boxes for high-pressure work has been thoroughly grasped, such details do not cause the slightest anxiety in the design of such equipment.

Returning to the compressor by Reavell, Fig. 7 shows the various gland boxes and packing devices. Taking firstly the first stage piston-rod packing, this is in two parts, viz. a metallic packing and a soft packing. The metallic packing is fitted each side of a lantern ring, and this ring is flooded with oil supplied by one of the reciprocating oil pumps driven from the crankshaft and as seen in Fig. 6. This oil is supplied at a pressure very slightly in excess of the pressure in the lower halves of the two first stage cylinders, and which is but little above that of the atmosphere. Any slight gas leakage from this gland is led back to the suction side of the compressor via a leakage indicator, which comprises a glycerine " bubbler " through which the gas must pass on its way to the suction side. The leakage indicator is seen on the gauge panel mounted in front of the cooling tank in Figs. 5 and 6.

The second and third stage cylinders are mounted over the two first stage cylinders, and any leakage past the rings of the higher stage pistons would find its way into the two low-pressure cylinders. This is prevented by fitting an oil seal to these two high-pressure cylinders, and the device comprises an oil connection from the mechanically driven oil pump to the mid point of the cylinders and arranged so that the piston does not overrun the hole. In this way the piston rings are well lubricated and oil sealed during the whole length of the stroke. This oil seal, together with the high speed of the machine, reduces leakage past the rings to an infinitesimal amount.

Relief valves are fitted to the various stages so that any excess of pressure may thereby be relieved.

Brotherhood Five-Stage Gas Compressor.

An example of a large hydrogen compressor by Peter Brotherhood of Peterborough is shown in Figs. 9, 10 and 11. It is designed for a throughput of 70,700 cu. ft. of free gas per 24 hours (2900 cu. ft. per hour) and the final delivery pressure is 400 atms. The speed of the machine is 250 r.p.m.

The compressor is of the five-stage type, with three cranks. The third stage cylinder is superimposed on the first stage cylinder, and the fourth stage cylinder over the second stage and the fifth stage cylinder is separate. In this case the cylinders are mounted on a massive entablature attached to the crank chamber by means of hollow pillars and through bolts. The crankshaft rotates in five adjustable bearings, and all motion parts within this crank chamber are lubricated by oil pump. The cross-heads work in flat slides, and both ends of the connecting rods are fitted with adjustable bearings. The piston-rods of all stages are fitted with soft packing rings, each with a lantern ring supplied with oil at appropriate pressures. The first and second stage pistons are fitted with ordinary sprung-on cast-iron piston rings. The third and fourth stage pistons are fitted with cast-iron carrier rings and piston rings alternately, and these are secured to the piston plunger rod by means of lock nuts, as shown. Lubricating oil is fed under pressure to the centre of the third and fourth stage cylinders, and matters are so arranged that the oil hole is covered by one portion of the piston at all parts of the stroke. The fifth stage piston is a plain plunger, and the packing for this comprises a long metallic gland with a lantern ring in the centre. The soft ring packing at the foot of this long metallic gland is under but very slight pressure, as there is a drain provided immediately above it for escape of oil which has seeped down the plunger piston.

All the soft and the metallic packings are fed with oil at appropriate pressure from a mechanically driven oil pump.

Since all the stages are single acting, the cylinder spaces beneath the first and second stage pistons are coupled to the suction side of the machine, and the second stage suction respectively, so that excessive pressure of gas due to leakage past the piston rings cannot develop. The first and second stage cylinders are lubricated by oil pump connection to the tops of each of these cylinders. Relief valves are fitted to all stages to ensure quick release of over pressure. The cylinders are enclosed in a water-cooling tank, and the gas compressed between each stage is cooled by steel pipe intercooling coils, also immersed in a water tank.

A photograph of this machine is seen in Fig. 9.

Brotherhood Four-Stage Oxygen Compressor.

A very interesting compressor, also by Peter Brotherhood, is the one shown in Fig. 12. It is for the compression of oxygen to a pressure of 240 atms., and the capacity of the machine is 1000 cu. ft. of free gas per hour. In compressing oxygen, lubricating oil of any kind cannot be used, and the only lubricant possible is good clean water. The design, therefore, is quite different from the machine for hydrogen just described.

The compressor is of the four-stage open type, i.e. the crankshaft is exposed, and the four cross-heads are fitted to single open slides. The cylinders are all of gun-metal, and the third stage is lined with a

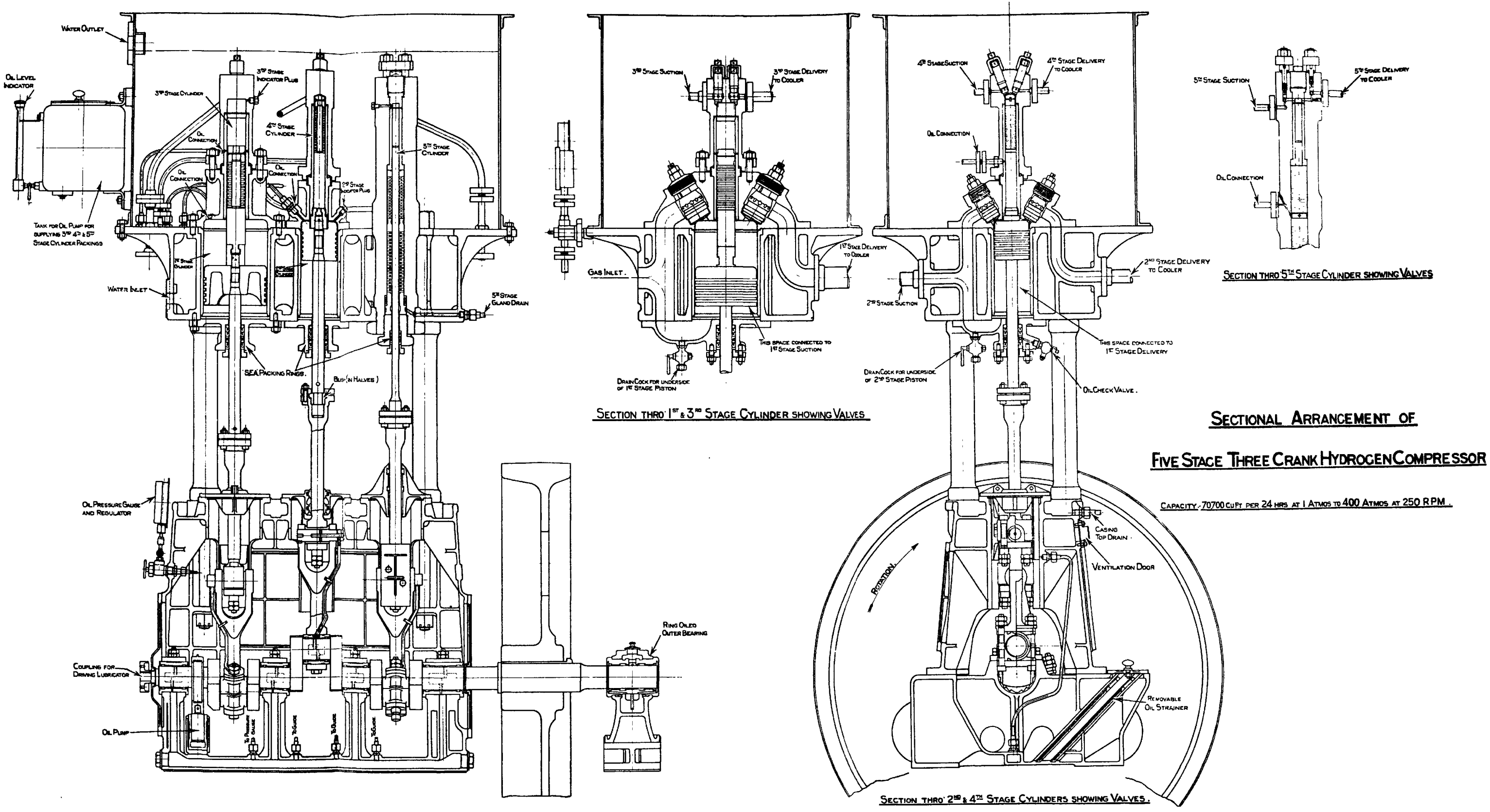

Water Outlet
Oil Level Indicator
Tank for Oil Pump for supplying 3rd 4th & 5th Stage Cylinder Packings
3rd Stage Cylinder
3rd Stage Indicator Plug
4th Stage Cylinder
5th Stage Cylinder
Oil Connection
Oil Connection
Oil Connection
2nd Stage Indicator Plug
1st Stage Cylinder
2nd Stage Cylinder
Water Inlet
5th Stage Gland Drain
S.E.A. Packing Rings.
Bush (in Halves)
Oil Pressure Gauge and Regulator
Coupling for Driving Lubricator
Oil Pump
To Pressure Gauge
To Guide
To Guide
To Guide
Ring Oiled Outer Bearing
3rd Stage Suction
3rd Stage Delivery to Cooler
Gas Inlet.
1st Stage Delivery to Cooler
This space connected to 1st Stage Suction
Drain Cock for underside of 1st Stage Piston
Section thro' 1st & 3rd Stage Cylinder showing Valves
4th Stage Suction
4th Stage Delivery to Cooler
Oil Connection
2nd Stage Suction
2nd Stage Delivery to Cooler
This space connected to 1st Stage Delivery
Drain Cock for underside of 2nd Stage Piston
Oil Check Valve.
Rotation.
Casing Top Drain.
Ventilation Door
Removable Oil Strainer
Section thro' 2nd & 4th Stage Cylinders showing Valves.
5th Stage Suction
5th Stage Delivery to Cooler
Oil Connection
Section thro 5th Stage Cylinder showing Valves
Sectional Arrangement of
Five Stage Three Crank Hydrogen Compressor
Capacity - 70700 Cu Ft per 24 hrs at 1 Atmos to 400 Atmos at 250 RPM.

Fig. 10.

Fig. 11.

Brotherhood hydrogen compressor.

[*To face page 44.*

stainless steel liner. The first and second stage pistons of gun-metal are fitted with hat leathers of oak tanned bark leather. The third stage

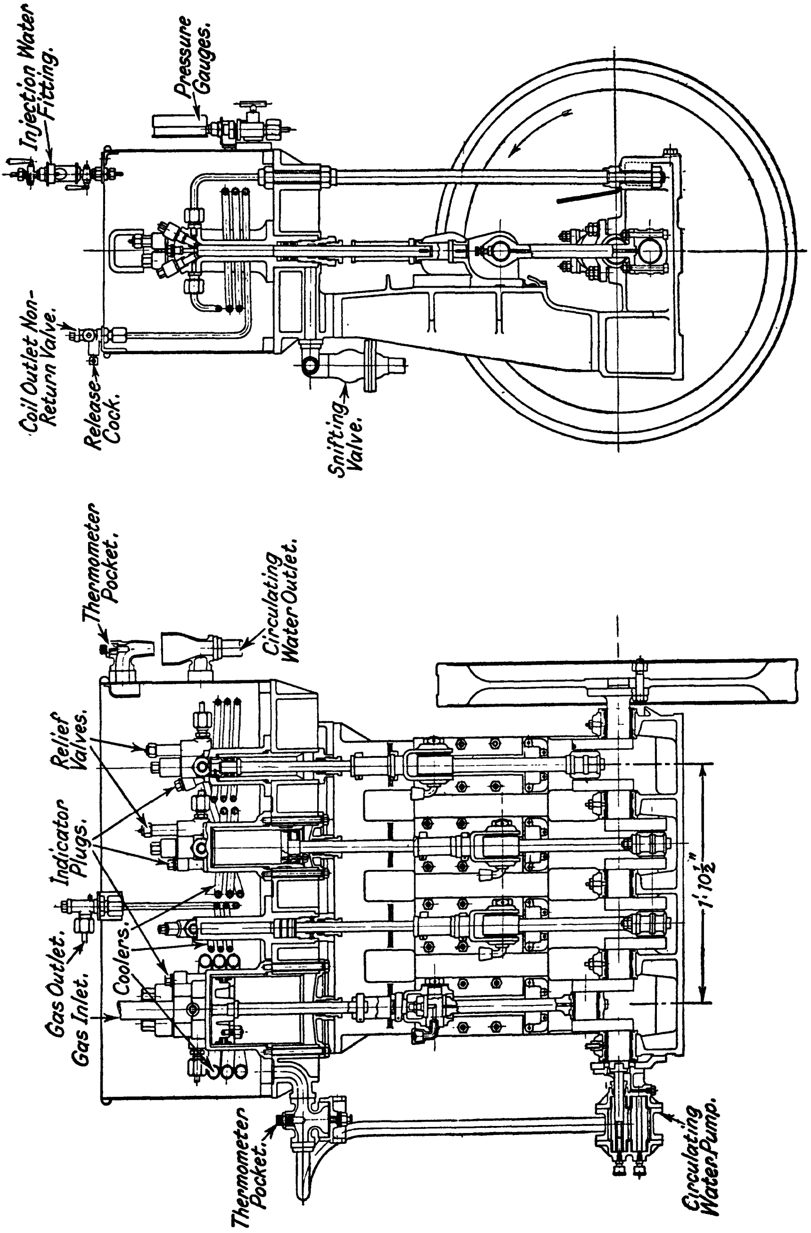


Fig. 12.—Brotherhood four-stage oxygen compressor.

piston is of phosphor bronze, and is fitted with two super-grey fibre cup rings. The fourth stage piston is of the plunger type made from stainless steel with lantern ring type of gland box, fed with water taken in at inlet. The side view of the machine shows this fourth stage plunger gland which is fitted with two super-grey fibre cup rings above the lantern. Beneath the lantern is fitted a little stuffing box of dry cotton packing, and this cotton packing is used for the first three stage cylinder piston-rods. All delivery valves are of the thimble type and the suction valves of the mushroom type. The valve seats are in monel metal and the valves in stainless steel. The valves are assembled complete before insertion in the valve boxes, in which they are held rigidly by heavy set screw and cap nut. The cylinders are all immersed with the interstage gas-cooling coils in a water-cooling tank fitted to the entablature. A photograph of a Brotherhood three-stage oxygen compressor of design similar to that described is shown in Fig. 13.

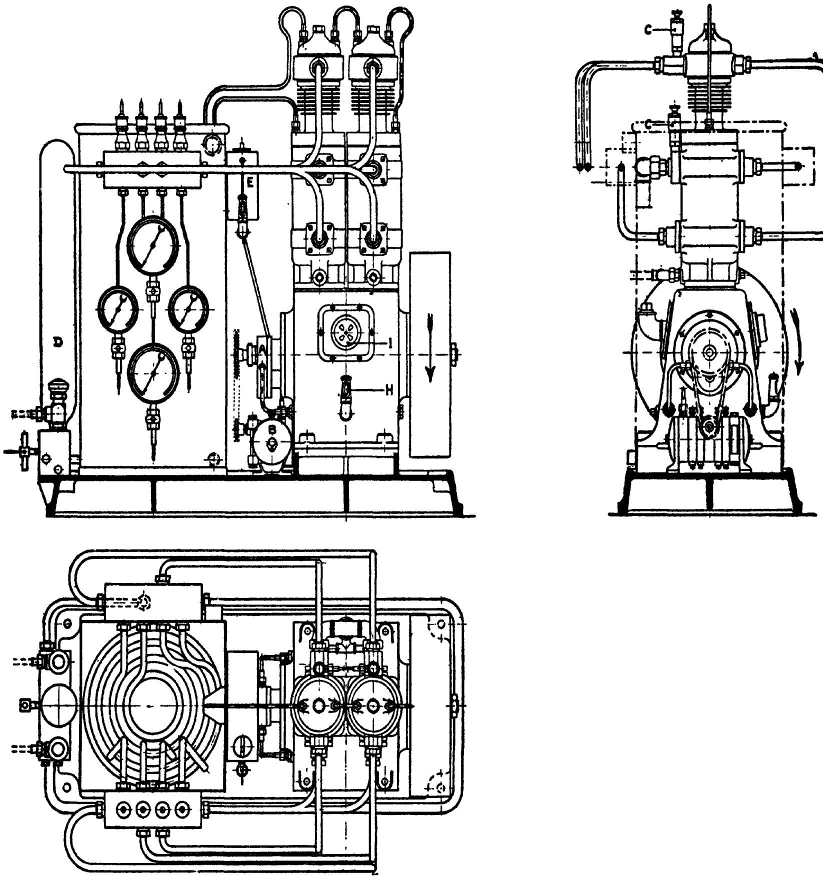
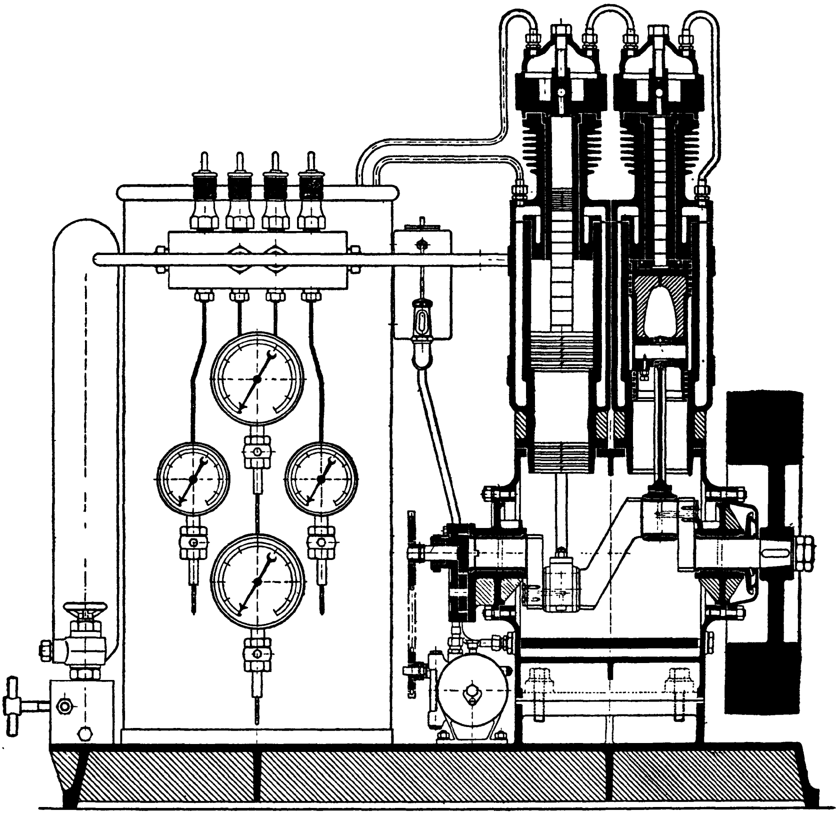


Fig. 14.—Luchard four-stage

Luchard Four-Stage Gas Compressor.

A high-pressure compressor by Luchard et Cie of Paris is shown in Figs. 14 and 15.

It is of the four-stage type for maximum pressures of 8540 lbs. per sq. in. (about 575 atms.). The two cranks are at 180°, and the third stage cylinder is over and in line with the first stage. The fourth is similarly located with regard to the second. All stages are single acting, and the speed of the machine is 340 r.p.m. The crank case is of cast iron, totally enclosed, with forced lubrication to all parts supplied by a gear pump at the end of the crankshaft. The first and second stage cylinders are of cast iron, bolted to the crank case, and the pistons therein are also of cast iron, with sprung-on piston rings. The connecting rods have adjustable big ends, white metal lined, and the small ends are bushed for gudgeon pins. The third stage piston is of steel, with cast-iron sprung-on



gas compressor.

rings, and the fourth stage steel piston is a plain plunger. The third and fourth stage pistons are fitted by a special patented arrangement to the first and second stage pistons respectively, to ensure alignment to the cylinders by allowing a little lateral movement. This is indicated in Fig. 14, in the section of the joint between the fourth and second stage pistons.

The high-pressure cylinders in the third and fourth stages are of special hardened cast bronze, with pressed in cast-iron liners. The first and second stage cylinders are cooled by water jacket, and the dome covers of the third and fourth stages are similarly cooled. The cylinder bodies of the third and fourth stages are air-cooled, and fins are arranged as shown in the drawing.

The second stage cylinder is lubricated by the gear type lubricator, which supplies oil to the working parts in the crank case. The first, third and fourth stages are lubricated by oil supplied by a special type of high-pressure oil pump driven from the crankshaft by a chain drive. (It is seen on the baseplate between the crank case of the compressor and the cooling tank.)

No packing is fitted to the piston of the fourth stage, as this is quite tight by virtue of the oil seal provided by the mechanically driven oil pump.

The gas between each stage is cooled by passing it through copper coils immersed in the cooling tank (to the left of the machine). The interstage gauges are fitted to the front of this tank, and the interstage safety valves are fitted in a common block at the upper part of the cooling tank. An oil separator high-pressure gas receiver is seen to the left of the cooling tank. A photograph of this machine is seen in Fig. 15. It deals with 9 cu. ft. per minute of free gas, and requires 13½ horse-power to drive it at the normal speed of 340 r.p.m.

Messrs. Luchard also manufacture a smaller machine for a final pressure of 1000 atms. (see Fig. 16).

The capacity of this machine is 2 cu. ft. of free gas per minute, and compression is carried out in four stages. It is very similar in outline and general design to that just described, except that the last three stage cylinders are all lubricated by entrainment of oil supplied to the first stage by a gear type of oil pump, which also serves to lubricate the moving parts of the crank chamber.

At a speed of 500 r.p.m. this 1000 atm. compressor absorbs 4 horse-power.

Hofer High Pressure Gas Compressors.

A complete range of high-pressure apparatus, especially suitable for laboratory and small manufacturing scale, is made by Andreas Hofer of Mulheim-Ruhr, who was for many years technical assistant

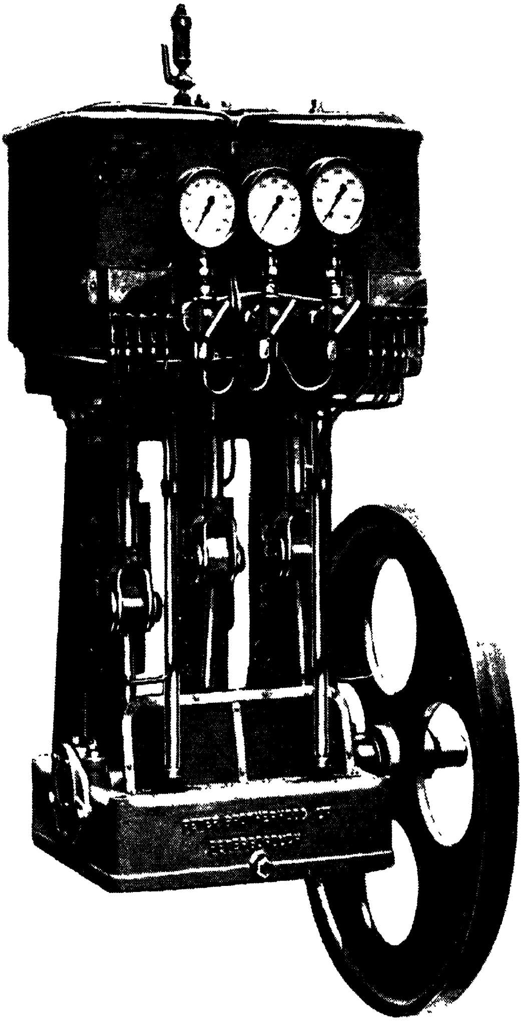


Fig. 13.—Brotherhood three-stage oxygen compressor.

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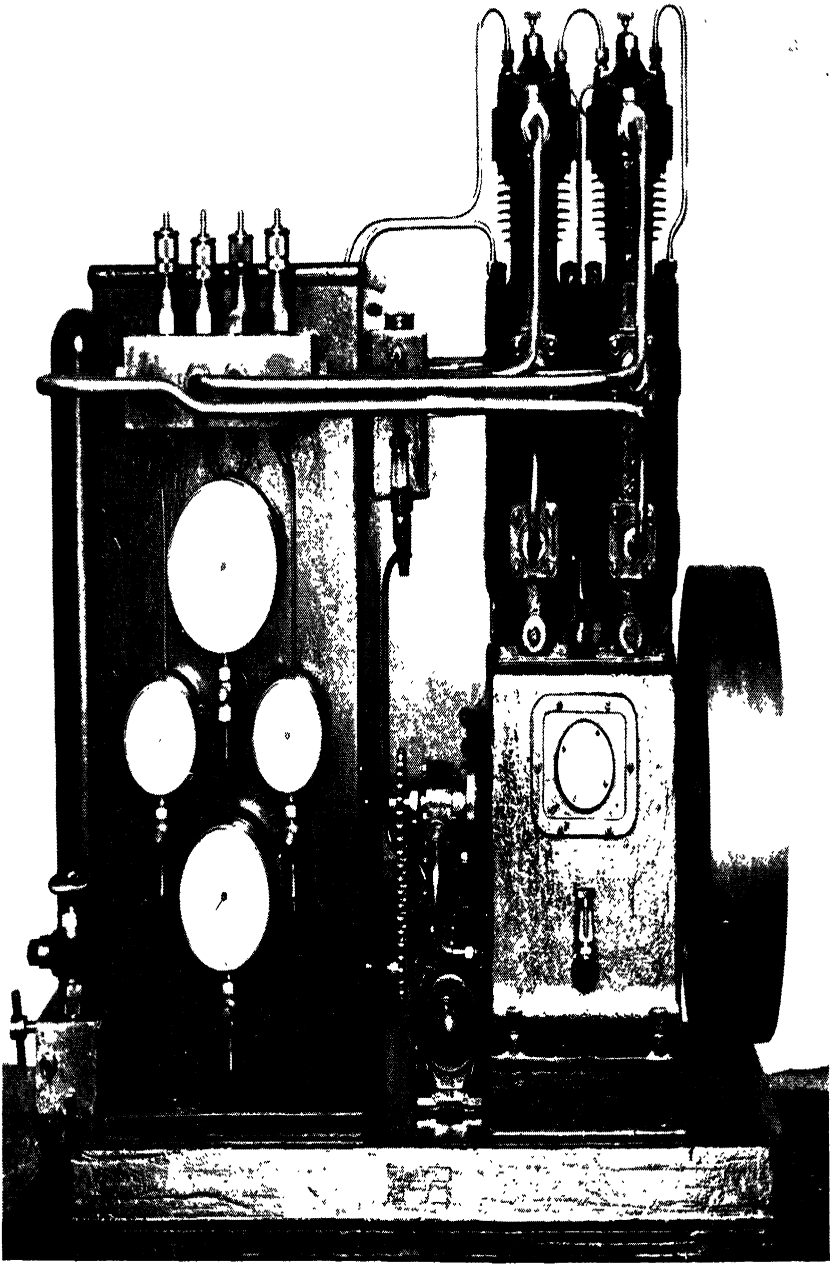

FIG. 15.—Luchard four-stage 575 atm. gas compressor.

[*To face page* 49.

to Dr. Franz Fisher at the Kaiser-Wilhelm Institute in that town. Included in this range is a series of gas compressors, suitable for the compression of gas from ordinary pressures up to 1000 atms., and capable of handling volumes of 0·15 cu. metres to 40 cu. metres—about 1400 cu. ft.—of free gas per hour. The smallest machine made by Hofer is of the two-stage type, and will compress gas to 70 atms. For 1000 atms. pressure five stages are used, and Fig. 17 shows a section of such a machine designed for a throughput of 10 cu. metres, or 350 cu. ft., of free gas per hour. Under such conditions, 5·5 kw. is required to drive the machine, which runs at a speed of 300 r.p.m. The quantity of cooling water required per hour is 0·2 cu. metre.

As seen in Fig. 17, the first stage is double acting, and the remainder are single acting. The first stage piston is fitted with sprung-on piston rings, the second, third and fourth stage pistons are fitted with cast-iron carrier rings and piston rings, and the fifth stage piston is of the plunger type. This piston is fitted with a long packing of white metal rings, and adjustment of this packing is made by removing the cap nut and the long bronze bush which is a sliding fit in the cylinder, and inserting a thin washer of brass, say, ·002-·003 in. thick against the white metal rings where shown. On replacing the long bronze sleeve and pulling home the cap nut, the white metal is compressed to an extent depending upon the thickness of the brass washer.

All cylinders are of Siemens-Martin steel, and water jackets are shrunk on as shown. Water is supplied under slight pressure to the first stage jacket, and is piped thence to all cylinder jackets.

All external parts of the machine, except the piston-rod gland, are mechanically lubricated by a chain-driven pump fitted as shown. The first cylinder only is lubricated, and the rest receive lubrication by entrainment of this oil in the gas flowing through the machine. Oil and water are removed from the final stage delivery by means of the oil separator shown. The piston-rod gland, which is of the lantern type, is lubricated by an oil bottle, which is maintained at the same pressure as the second stage delivery by a pipe taken from this stage to the top of the bottle. (The nipple provided for this purpose is shown at the top of the bottle.)

The gas between each stage is cooled by passing the gas through copper coils inserted in the water-cooling tank seen at the front of the machine.

Pressure gauges are fitted to each stage, and when running under full pressure (i.e. 1000 atms. final delivery pressure) the first stage delivery should be at 2½ atms., the second at 10-15 atms., the third 60-80 atms., the fourth 250-275 atms., and the fifth, of course, at 1000 atms. (In this connection note that the permanent gases become less compressible as the pressure rises above 100 atms. or so.)

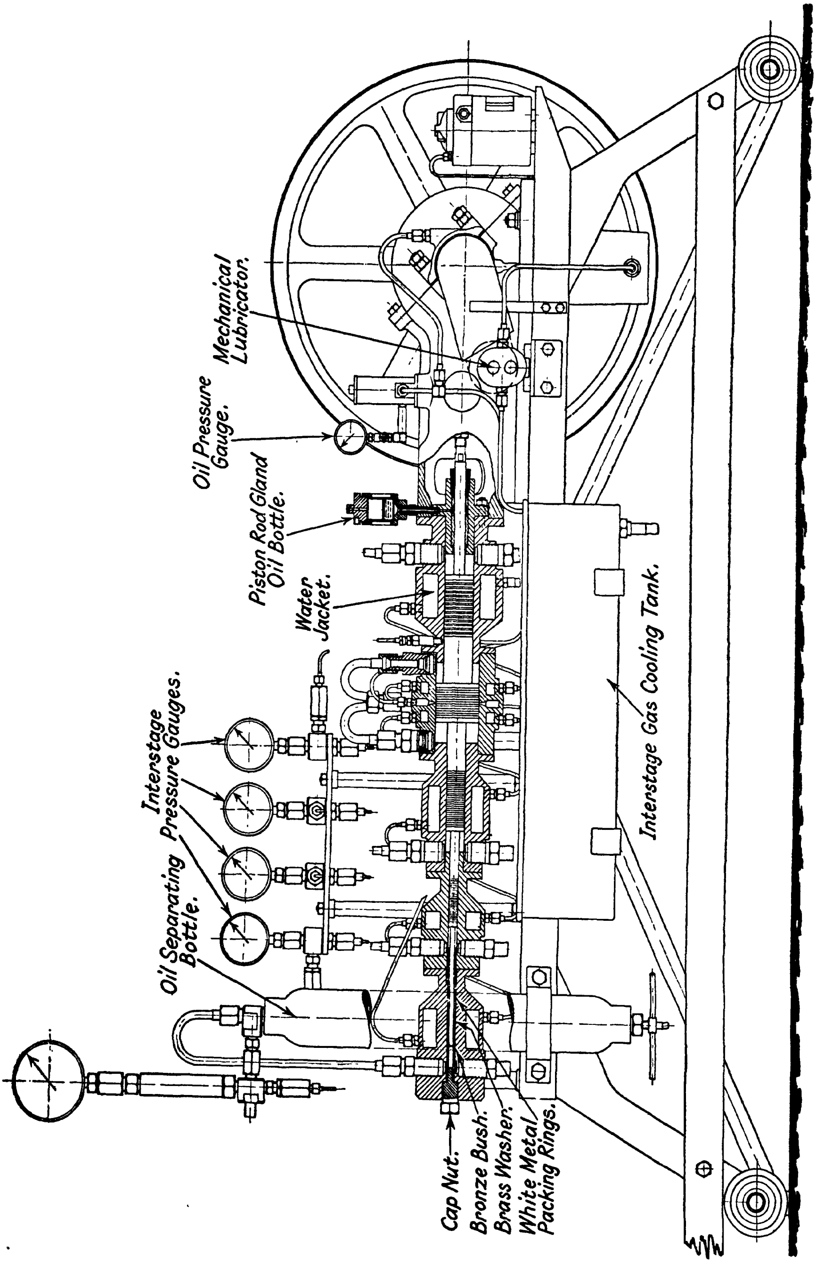
Mechanical Lubricator.
Oil Pressure Gauge.
Piston Rod Gland Oil Bottle.
Water Jacket.
Interstage Pressure Gauges.
Oil Separating Bottle.
Interstage Gas Cooling Tank.
Cap Nut.
Bronze Bush.
Brass Washer.
White Metal Packing Rings.

FIG. 17.—Hofer five-stage 1000 atm. gas compressor.

It is worthy of note that by arranging the second stage cylinder "next to the atmosphere" and thus maintaining the piston-rod

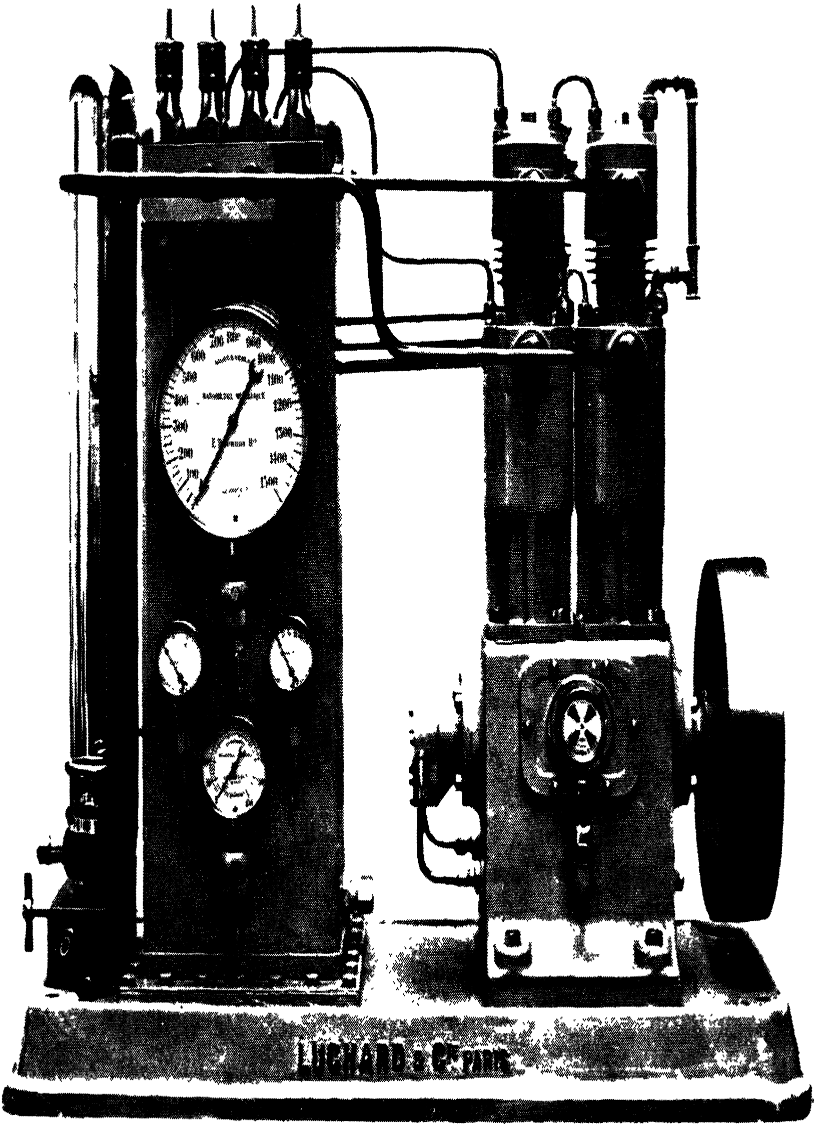

Fig. 16.—Luchard four-stage 1000 atm. compressor.

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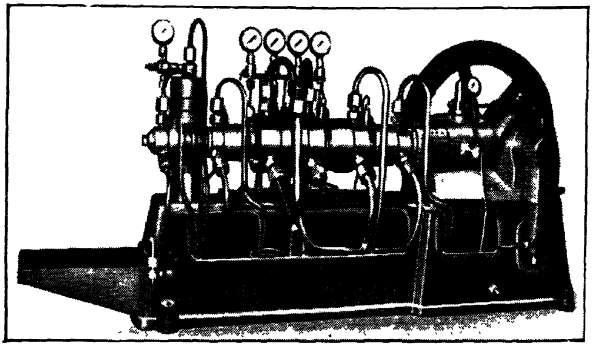


FIG. 19.—Hofer five-stage 1000 atm. gas compressor.

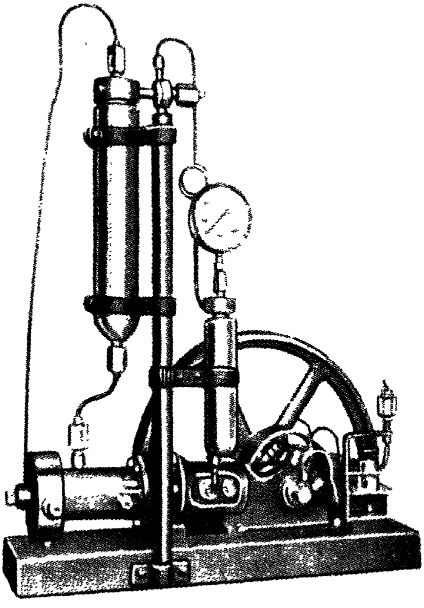


FIG. 20.—Hofer single-stage 2000 atm. supplementary compressor.

[*To face page* 51.

packing under positive gas pressure, there is no danger of air leakage into the compressor, as would be the case were the piston-rod under suction at any time.

All valves of Hofer compressors are of similar type, and a view of a typical valve taken apart is shown in Fig. 18. It will be noted that they are of the flat plate type, seated on a flat surface which is of small area.

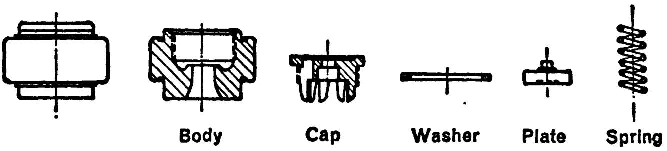


FIG. 18.—Details of valves of Hofer compressors.

Interstage relief valves are fitted to all stages, in order to prevent overpressure in case of accident to a valve or piston packing.

A photograph of a large Hofer five-stage machine is shown in Fig. 19. It is much bigger than that just described, and has a capacity of 36 cu. metres, or over 1000 cu. ft. of free gas per hour.

Compression of small Volumes of Gas to very High Pressures.

Hofer also supplies a one-stage supplementary compressor which is capable of raising the pressure of the permanent gases from 1000-2000 atms. It is of the single acting plunger type, and a photograph of this one-stage machine is seen in Fig. 20.

Whilst dealing with the subject of supplementary compressors, it is perhaps convenient to make reference to the technique developed for obtaining very high pressures (5000-20,000 atms.). For example, Bridgman's method comprises compression by means of standard equipment to 2000 atms., and then completing the remainder of the compression desired by one stroke of a plunger, the piston of which is packed in a special manner which embodies Bridgman's "unsupported area" principle. Fig. 21 shows the method adopted.

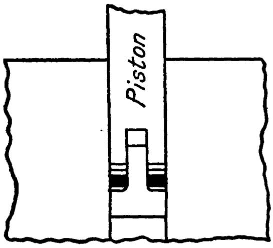


FIG. 21.—Bridgman's method of packing high-pressure pistons.

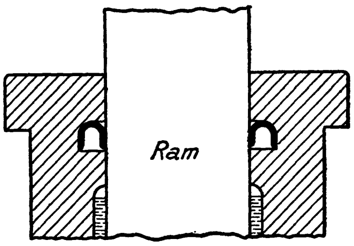
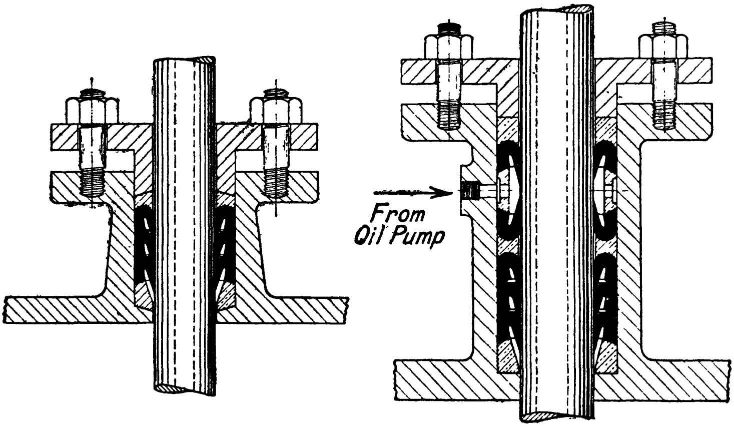


FIG. 22.—"U" leather hydraulic packing.

The stem of the cheese head plug projects into the hole in the end of the hardened steel plunger, and it is this stem which constitutes the unsupported area. The pressure intensity in the soft packing (indicated by the blacked area) is greater than that of the liquid in the cylinder in the ratio of the areas of the annular space and the head of the plug. The soft packing recommended is rubber, which is supported by discs of copper and soft steel. For plungers of $\frac{1}{2}$-inch diameter, Bridgman recommends a thickness of rubber of $\frac{1}{8}$ in., and a lubricant such as vaseline between the faces is advisable. This type of packing was recently employed by Bone, Newitt and Townend in the measurement of explosion pressures of the order of 10,000 atms., and found to be satisfactory (*Proc. Roy. Soc.*, 1933, A, **139**, 57).

It is interesting to compare this type of packing as developed by



A. FIG. 23. B.

Bridgman for high hydraulic pressures with that invented by Bramah over one hundred years ago, in connection with hydraulic press work.

Leakage between a moving ram and the walls of a hydraulic cylinder is prevented by means of a " U "-shaped leather, or flexible ring, which is kept in contact with each side by the internal fluid pressure. Fig. 22 will illustrate this. When the cup leather is large it is provided with an internal brass former ring. The friction of such packing is of course not negligible, and experiments described in *Engineering* in 1888 gave the loss due to friction as 4-9 per cent. of the ram pressure for leathers in good condition. In one bad case the loss due to friction was as high as 20 per cent. of the ram pressure.

A modern development of the Bramah cup leather is the S.E.A. ring marketed by Trist & Co. of London. It is again a type of packing well suited to hydraulic work, as illustrated in A, Fig. 23, or it can be used for cases where gas is being handled at high pressure by employing the lantern ring type of stuffing box (B, Fig. 23), the principle of which has already been described. The principle of the S.E.A. ring is the same on that of the Bramah ring, i.e. the fluid pressure exerted forces the lips of the ring against the bearing surfaces of the fixed and moving parts and hence is " self sealing."

Poulter, of the Department of Physics, Iowa Wesleyan College, has developed another type of plunger packing for very high pressures, and which is simplicity itself. It consists of a plain solid cylindrical rubber bung, which is forced down the cylinder by means of a close fitting piston. A combined autoclave-compression unit recently built by Imperial Chemical Industries for carrying out chemical reactions at high pressure incorporates Poulter's suggestion, and it is stated to be quite satisfactory at pressures up to 12,000 atms. This autoclave plant is described fully in Chapter VIII.

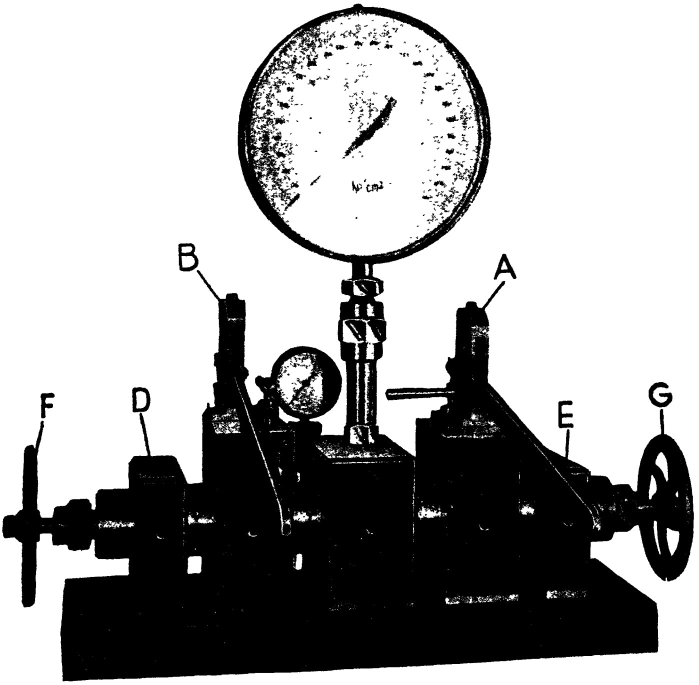


FIG. 24.—Michel-Kipp 5000 atm. press or oil pump.

Michels of Amsterdam has developed a displacement method of compression which is shown in Figs. 24, 25 and 26. The compression is carried out by means of oil as the working fluid. The required oil pressure is obtained by an intensification of a low pressure generated by a hand lever pump. In the standard type the pressure given by the lever pump is about 300 atms., and that delivered by the hydraulically driven plunger is 2500 atms. The model shown in Fig. 24 is for a maximum pressure of 5000 atms.

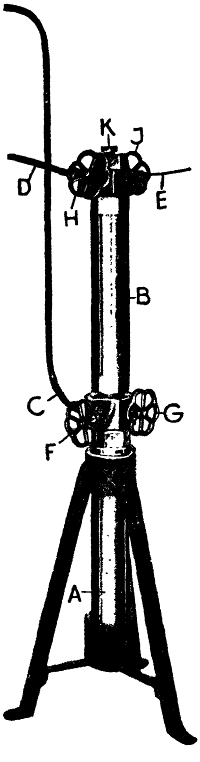


FIG. 25.—Michel-Kipp high-pressure gas compressor.

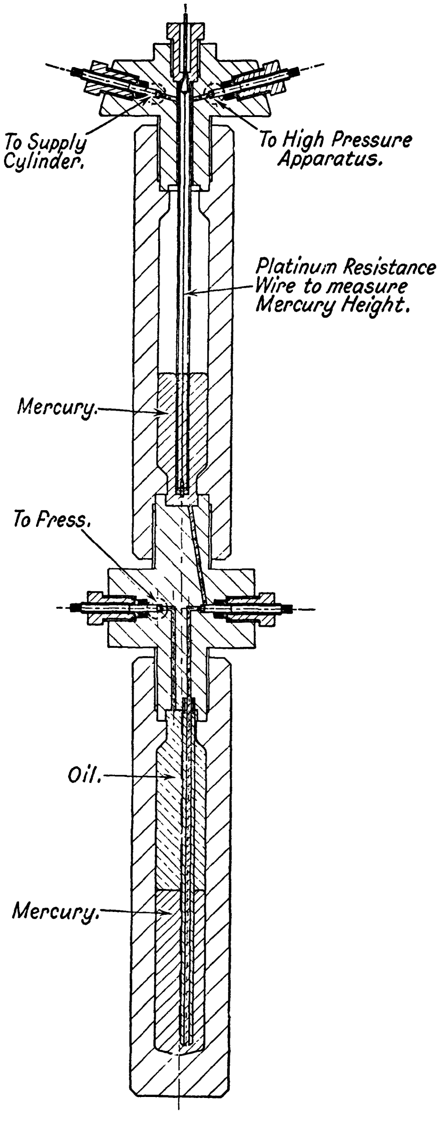

To Supply Cylinder.
To High Pressure Apparatus.
Platinum Resistance Wire to measure Mercury Height.
Mercury.
To Press.
Oil.
Mercury.

FIG. 26.—Michel-Kipp 2500 atm. gas compressor.

The actual gas compressor designed by Michels is shown in Figs. 25 and 26. This apparatus has the advantage that the gas comes into contact with mercury only, and not with oil.

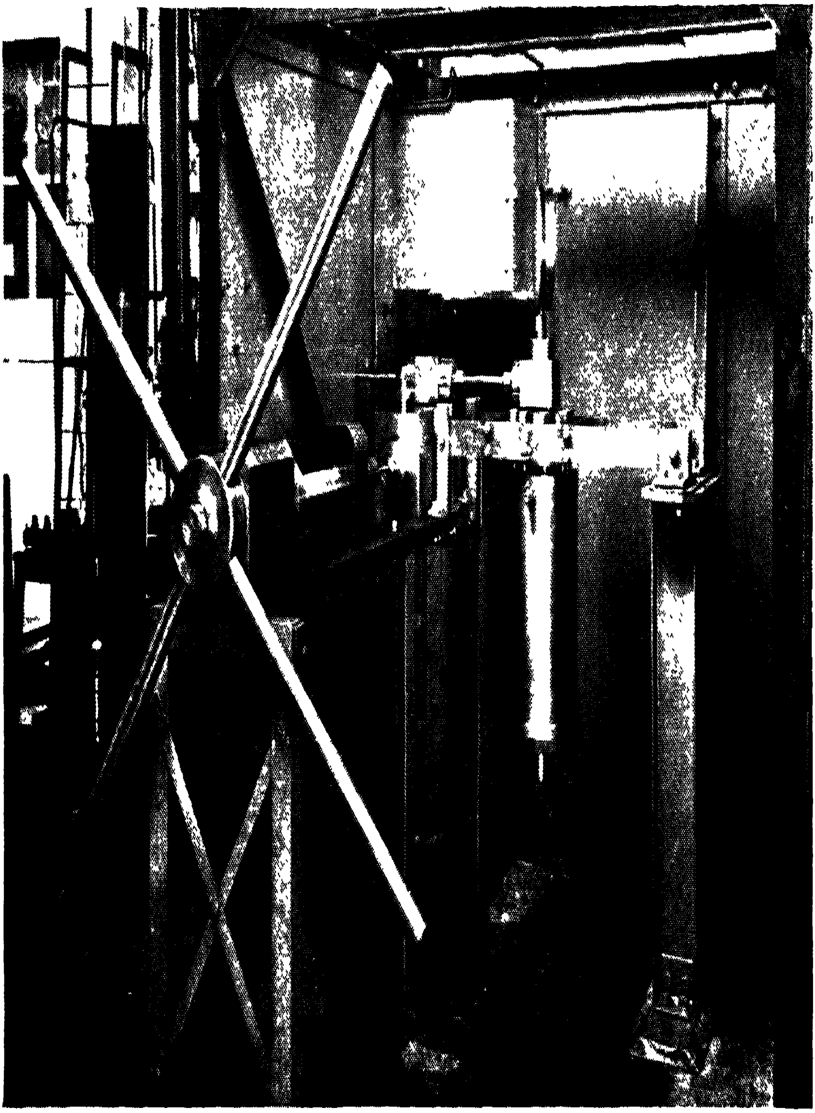


FIG. 28.—C.R.L. 3000 atm. compression pump and autoclave.

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The connection C is to the high-pressure oil pump, D to the cylinder containing gas (say at 120 atms.), and a connection E is coupled to the vessel into which the compressed gas is to be delivered.

The lower part of the compressor is filled with mercury. If pressure is applied to this mercury, it rises through the inner tube to the upper space B if the valve F is open, and so the gas is driven out at E. The opening C may be shut off by valve G, the connection between A and B by valve F, the inlet side D by valve H, and the high pressure side E by valve J. By alternately opening the valves concerned, new quantities of gas can be admitted, and compressed. In order to check the mercury level at B an electric indicator is fitted as shown.

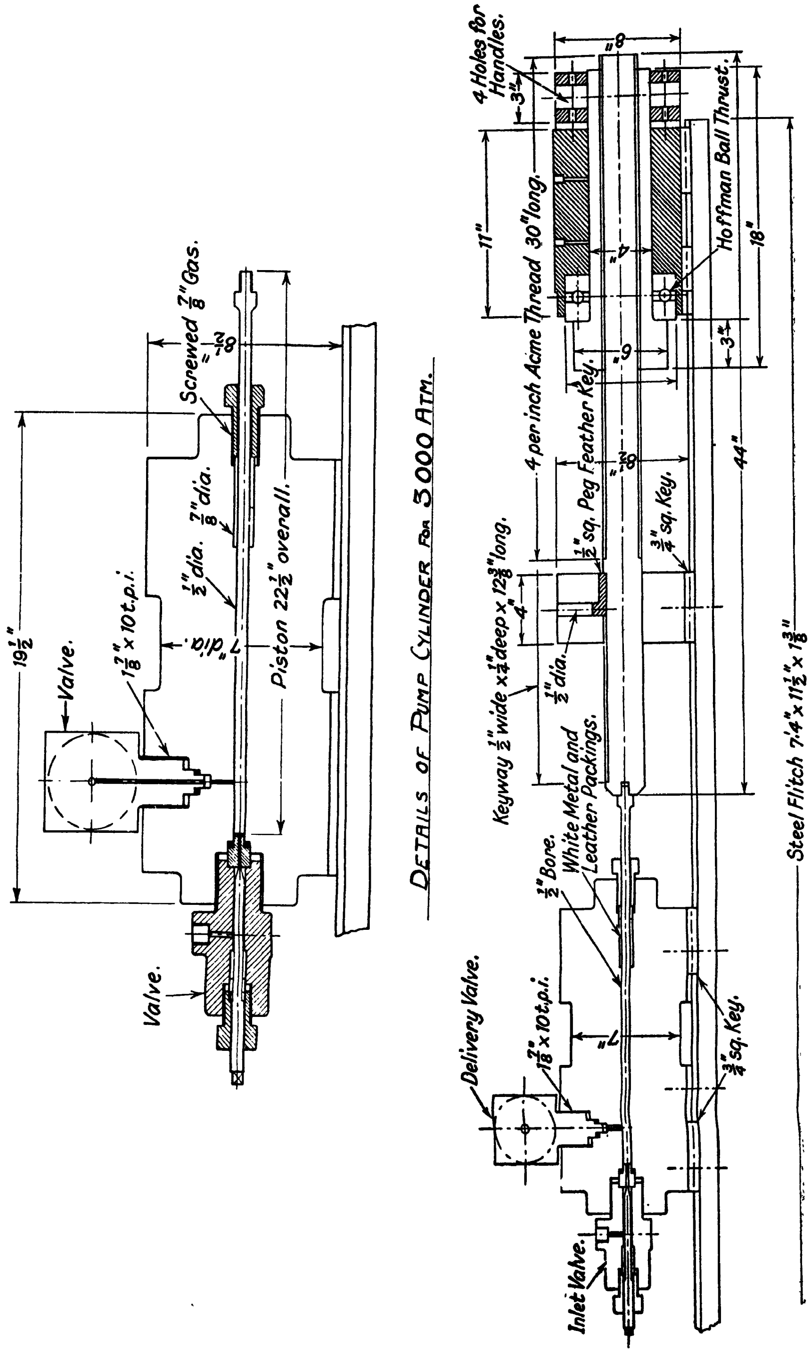
A screw gas compression pump for pressures up to 3000 atms. has recently been constructed at the Chemical Research Laboratory, and it is shown in Figs. 27 and 28. The construction is clear from the drawing, and it has been designed for use with the autoclave described in Chapter VIII., and which is seen on the right of the pump in the photograph. The piston packing is composed of groups of leather rings (three rings each $\frac{3}{16}$-inch. wide, separated by white metal washers each $\frac{1}{4}$-inch wide). The valves are of the screw-down pattern, and are hand operated (see Chap. V.).

LARGE COMPRESSORS.

In handling very large volumes of gas for processes such as the Haber-Bosch, it is sometimes convenient and economical to use separate machines each raising the pressure in stages. For example, Figs. 29 and 30 show two large compressors made recently by Peter Brotherhood of Peterborough for such work. A mixture of nitrogen-hydrogen at a pressure of 10 atms. is supplied by a low-pressure compressor to the intermediate pressure reciprocating compressor shown in Fig. 29.

This intermediate reciprocating compressor raises the pressure of the mixed gases from 10 atms. to 55 atms. The machine is of the three-crank type, and there are three sets of two-stage compression cylinders, each set being identical in duty and dimensions. The speed of the machine is 120 r.p.m., and the capacity (reduced to N.T.P.) is 36,650 cu. metres per hour (or nearly 1,300,000 cu. ft.), raised from a pressure of 10 atms. to 55 atms. The cylinders are of cast steel, and are single acting. The diameter of the first stage cylinder is 2 ft. 3 ins., and the second stage 1 ft. 5 ins. The stroke is 24 ins. The machine absorbs 3500 horse-power.

The machine generally follows Brotherhood's standard design for high-pressure compressors, i.e. the crank case is totally enclosed, and forced lubrication is used to all crank case parts such as main


Valve.
$19\frac{1}{2}''$
Valve.
$1\frac{7}{8}''\times 10$ t.p.i.
$7''$ dia.
$\frac{1}{2}''$ dia.
$\frac{7}{8}''$ dia.
Screwed $\frac{7}{8}''$ Gas.
$\frac{7}{8}''$
Piston $22\frac{1}{2}''$ overall.
Delivery Valve.
Inlet Valve.
$\frac{7}{8}''\times 10$ t.p.i.
$\frac{1}{2}''$ Bore.
White Metal and Leather Packings.
$7''$
$\frac{3}{4}''$ sq. Key.
Keyway $\frac{1}{2}''$ wide $\times\frac{1}{4}''$ deep $\times 12\frac{3}{8}''$ long.
$\frac{1}{2}''$ dia.
$4''$
$\frac{1}{2}''$ sq. Peg Feather Key.
$\frac{3}{4}''$ sq. Key.
$2\frac{1}{2}''$
4 per inch Acme Thread 30'' long.
$6''$
$4''$
$11''$
$3''$
4 Holes for Handles.
$8''$
Hoffman Ball Thrust.
$18''$
$3''$
$44''$
Steel Flitch $7'4''\times 11\frac{1}{2}''\times 1\frac{3}{8}''$

DETAILS OF PUMP CYLINDER FOR 3000 ATM.

FIG. 27.

bearings, crank pins, cross-heads, etc. The cylinders are secured to the entablature and crank case by eight massive hollow steel pillars with through bolts, and the cylinders are immersed in a cooling tank supported from the entablature. First-stage compression is on the downward stroke, and second-stage compression on the upward stroke. Both pistons are of cast iron with sprung-on piston rings. All pistons are efficiently lubricated under pressure by oil ports in the centre of the cylinder, as shown in the drawing. These oil ports are always covered by one portion of the piston throughout the whole of its movement, and as the oil is supplied under pressure by a mechanical oil pump, this serves as a very effective method of sealing the piston.

The first stage valves are mounted in circular cages which fit inside valve tunnels at each side of the bottom of the cylinder. These valves are arranged in sets of three, and there are four sets to each valve cage. The whole of the cage can be withdrawn as a complete unit. The valves are of the light plate type. The second stage valves are also mounted in cages, of which there are two suction and two delivery sets. These are mounted in circular valve housings in the head of the cylinder. These valves again are of the light plate type.

The piston-rods are each fitted with two stuffing boxes. The first are long metallic packings with lantern ring lubricators and oil seals, and the second stuffing boxes are of the soft non-metallic type, and serve merely to provide small chambers into which the oil seeping down the rods can collect. A waste-oil escape pipe is fitted to each of these latter stuffing boxes. Safety valves are fitted to each of the cylinder delivery boxes, and the escape from these is led into the suction side, so that there is no loss of gas in case of slight leakage past these valves.

The machine just described raises the gas pressure from 10 atms. to 55 atms., and the next and final stages of compression are carried out in the machine shown in Fig. 30. This is a two-stage machine, and raises the pressure of the gas from 50 atms. to 260 atms. It is of the 3-crank type, with three similar sets of cylinders which are 11½ ins. and 6 ins. diameter. The stroke is 2 ft. 0 ins. The suction capacity of the machine (measured at N.T.P.) is of the order of 24,800 cu. metres per hour (875,000 cu. ft.). The speed of the machine is 120 r.p.m., and the horse-power required is 2300. The first stage cylinders are of cast steel, and the second stage of forged steel. The general arrangement of the machine is similar to the two-stage lower-pressure machine just described. The crank case is totally enclosed, and "force feed" lubrication is supplied to all bearing surfaces. The cylinders are again mounted on an entablature, which is supported from the crank case by eight

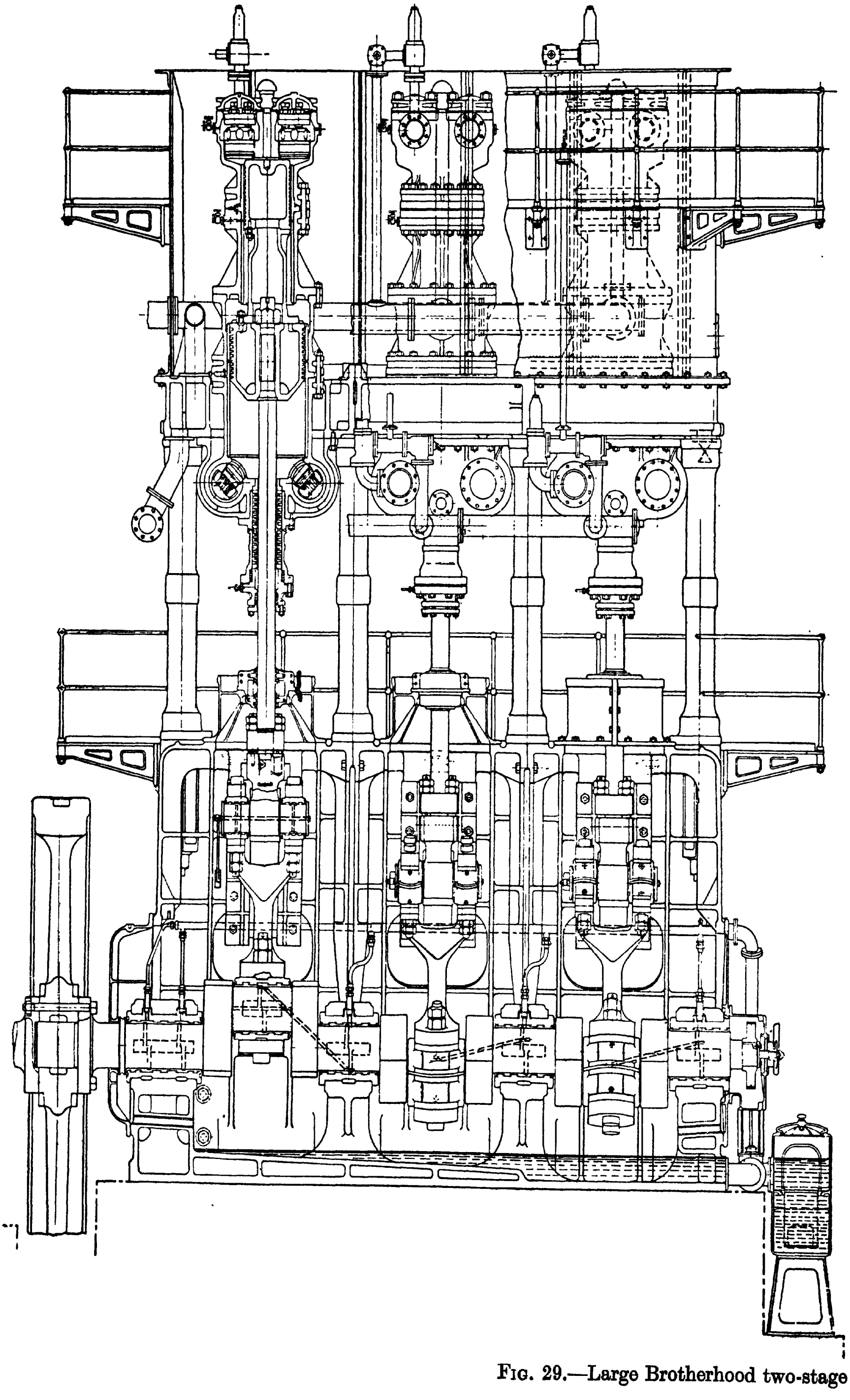
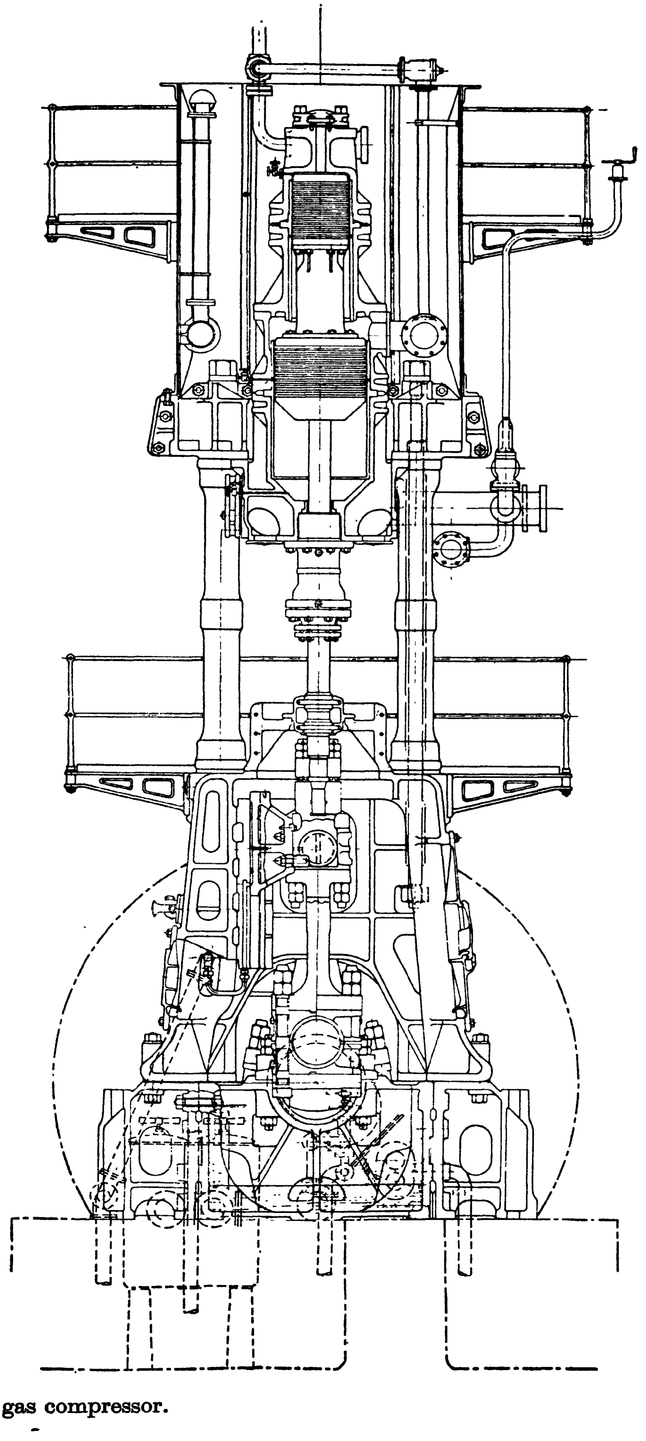


FIG. 29.—Large Brotherhood two-stage



55 atm. gas compressor.

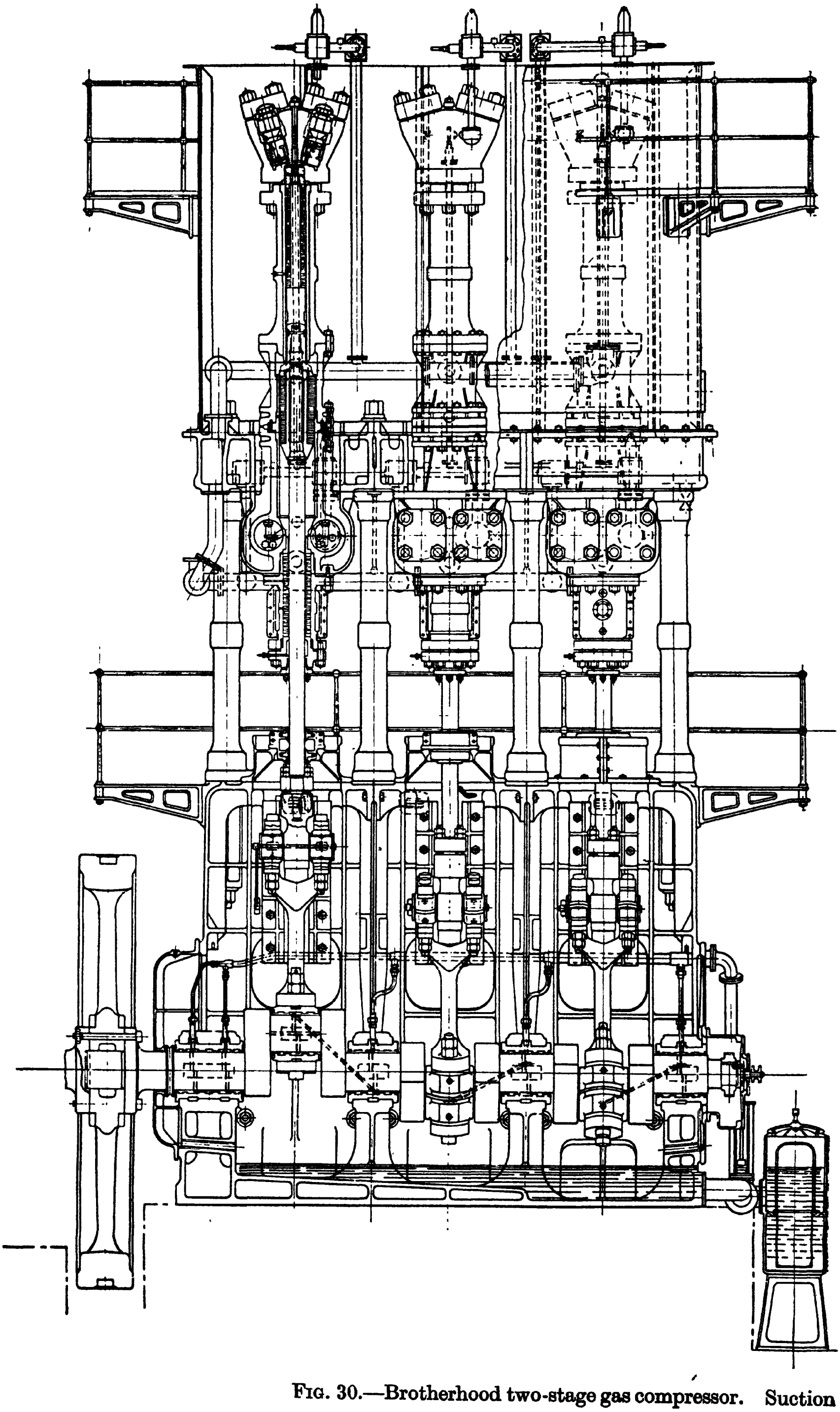
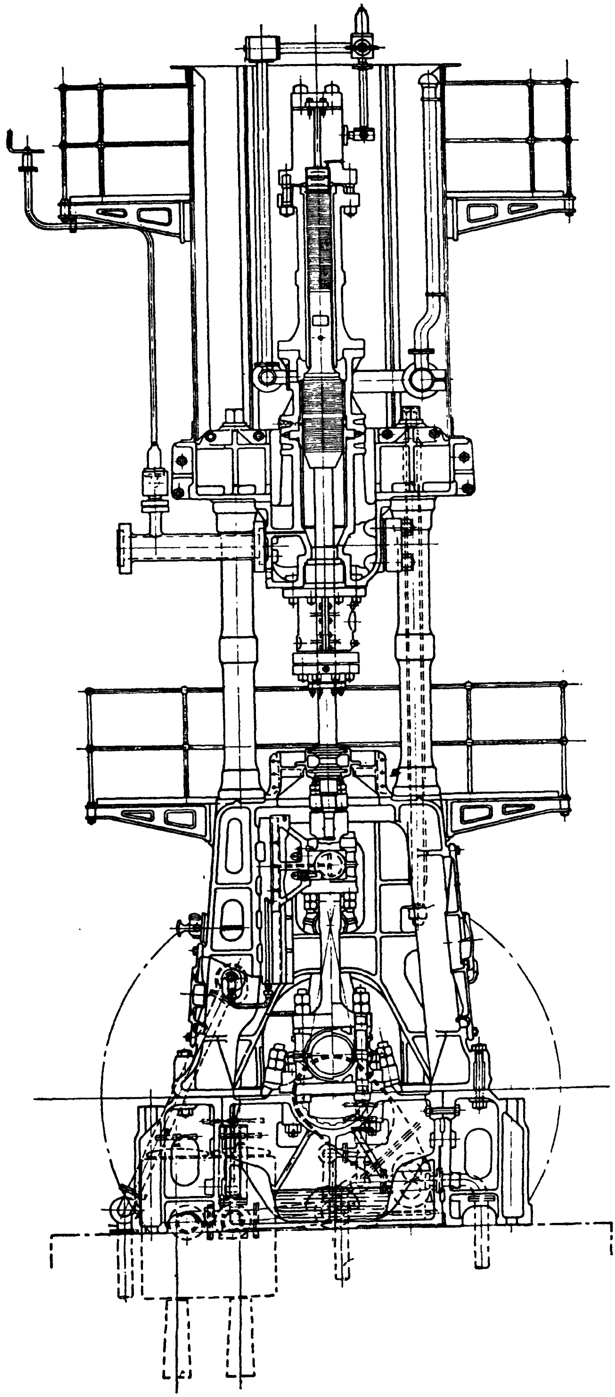


FIG. 30.—Brotherhood two-stage gas compressor. Suction



pressure—50 atms. Delivery pressure—260 atms.

hollow pillars and through bolts. The cylinders are wholly immersed in a water-cooling tank built on the entablature flange. The same type of lubrication and oil supply to the cylinders and piston-rods is also employed.

All cylinders are fitted with renewable hardened steel liners. This applies to both these two-stage compressors.

Sulzer 1000 *atm. Gas Compressor.*

The firm of Sulzer Brothers, Winterthur, some six years ago introduced a type which differs in many respects from those hitherto known, and which, it is stated, can claim for itself a number of advantages from an operating and technical point of view. The following remarks will serve to elucidate the principal characteristics of the Sulzer " hyper-compressor."

The starting-point of this development was the large Sulzer gas compressor for pressures up to 300 atms. ; these machines are constructed with as many as six compression stages, and, from a theoretical point of view, it would be sufficient to add a further stage to the 300 atmosphere machine, so as to obtain a pressure of 1000 atms. The dimensions of the extra cylinder would not by any means be unduly large, as the gas at 300 atms. already has a very small specific volume. The extra power necessary would also be very moderate, the increase being in proportion to the logarithm of the pressures. In actual practice, however, there is a great difference between working at a pressure of 300 atms. and at 1000 atms., since the gas at the higher pressure is so dense and heavy, and so changed in its chemical characteristics, i.e. with regard to attacking the material of which the compressors are made, that it was necessary to consider special methods of construction to cope with the altered circumstances. The fundamental characteristic of the Sulzer hyper-compressor is the vertical arrangement of the cylinders for the sixth and seventh stages ; these cylinders are operated hydraulically by means of columns of oil, and are referred to in the following description as hyper-stages, for brevity.

The design of the Sulzer hyper-compressor may be seen by referring to Figs. 31-39, which show the machines which were recently supplied to the Compagnie de Bethune, Bulley-les-Mines, which employs the Claude process for the manufacture of synthetic ammonia. Each compressor is designed to deal with an effective suction intake of 4000-4500 cu. metres per hour (2400-2650 cu. ft. per min.) at a final pressure of 1000 to 1100 atms. (14,200-15,650 lbs. per sq. in.). It is driven by a three-phase motor of the flywheel type, mounted on the shaft, the motor delivering a constant output of approximately 2000 h.p. at the normal speed of 122 revolutions per minute. Two such units had been laid down at the end of

1929, but it was intended to lay down a number of similar compressors for extensions. The machine has a two-throw crankshaft, the first, second and third stages being operated by one crank, and the fourth and fifth, together with the primary oil cylinder, by the other. All the horizontal cylinders are fitted with detachable and interchangeable cast-iron liners having the Sulzer type of fixing flange in the middle, so that expansion may take place freely towards both ends

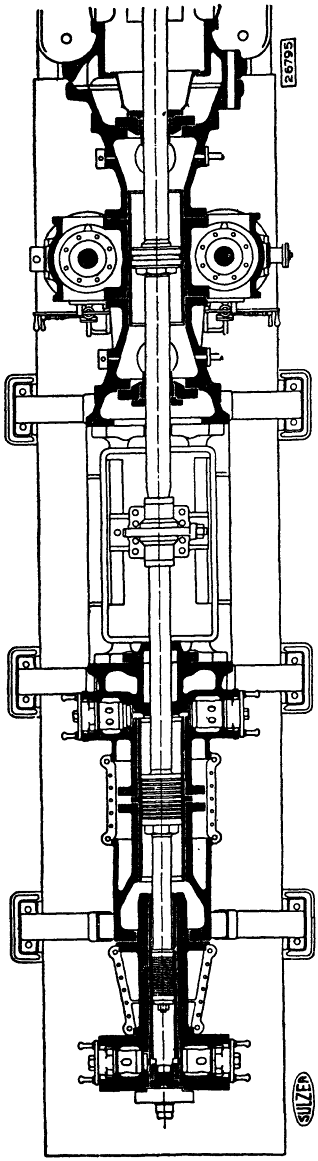


FIG. 31.—Horizontal section through third, first and second stages of Sulzer 1000 atm. compressor.

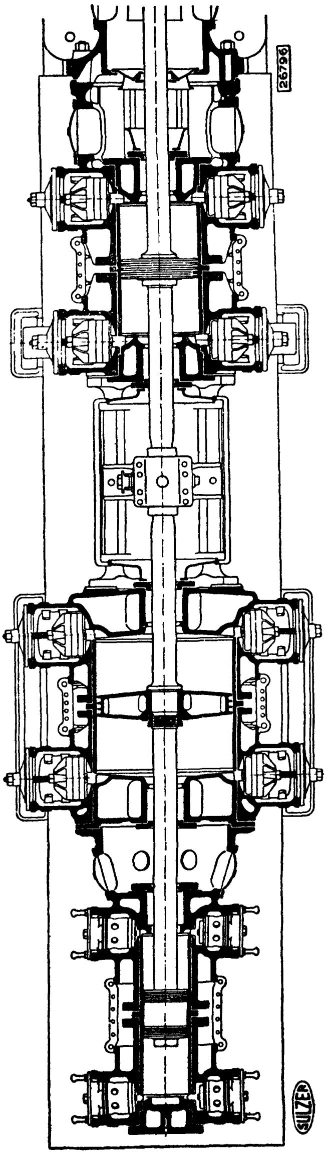


FIG. 32.—Horizontal section through fifth and fourth stages and the hydraulic drive of Sulzer 1000 atm. compressor.

of the cylinder. The cooling water jackets are made in two parts, thus providing the advantage of the water chambers being readily accessible at all times for cleaning, and also obviating as far as possible any indeterminate stresses in the cylinder walls, as would otherwise be the case with integral cooling jackets. The first and second stages, which are those having the largest bores, have disc pistons which float on the piston-rods and therefore cannot cause uneven wear on the cylinder walls. The piston-rod is made in two parts for each side of the machine, with a knuckle joint connection in the slipper between.

This arrangement facilitates erection and also brings the main bearing surfaces outside the cylinder, which ensures their being amply lubricated and easily accessible for attendance. Metallic packing of the Kranz type is used for all horizontal glands, and the glands themselves are arranged so as to be adjustable from the outside, easily taken up, and accessible for small repairs. The cylinders are mounted flexibly on the bedplate in so far that alterations of length consequent upon warming up, and the force of the piston can take effect freely, and for this purpose sliding surfaces, which may be lubricated, are provided under the cylinder feet. Spring loaded ring valves are used up to and including the fifth stage, their construction being of the ordinary and well-known type ; their chief characteristic is small weight, which enables them to

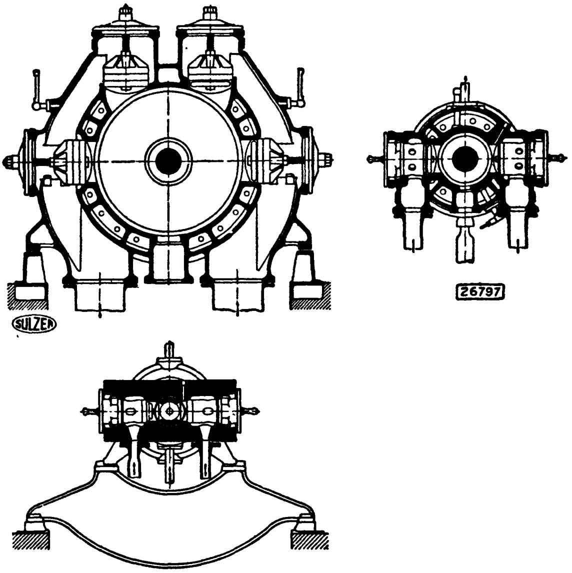


Fig. 33.—Cross-section through first, third and fifth stages of 1000 atm. Sulzer compressor.

operate silently and dependably even at a comparatively high rate of speed. The valve seatings may, if necessary, be divided up into a number of interconnected rings, which provide an opening of large cross-section with a very small lift, thereby providing a perfect indicator diagram. Breakage of the valves is infrequent, and the wear slight, by reason of the characteristics mentioned.

Mention should also be made of the four bearings for the crankshaft in two forked frames. Both the double cranks, as well as the entire gearing are enclosed in an oil and dustproof casing, lubrication being effected automatically from a large oil container located in the basement and provided with an interchangeable filter arrangement. Oil circulation is maintained by means of a gearwheel oil pump driven direct from the shaft. A separate forced lubricating reciprocating pump supplies oil to the cylinders and glands.

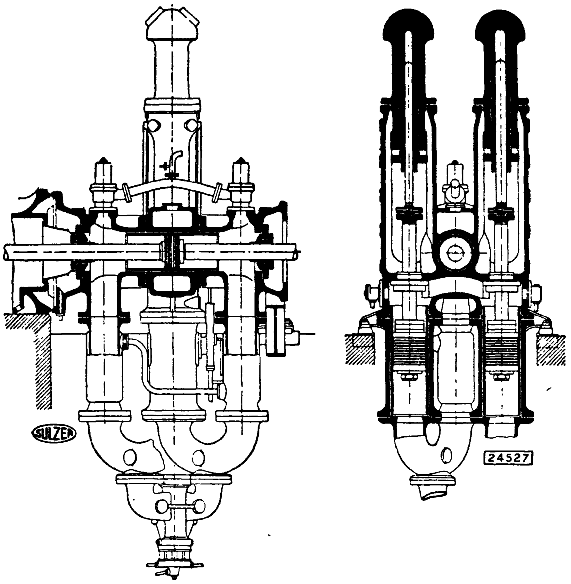


FIG. 34.—Hydraulic drive of sixth and seventh stages of Sulzer 1000 atm. compressor.

The chief item of interest in this machine, however, is the two hyper-stages, as already mentioned ; they are shown in section and elevation in Figs. 34 and 35. The primary oil cylinder is fitted between the frame and the cylinder for the fourth stage on the high-pressure side of the machine, whilst the secondary oil cylinders stand at both sides of the primary oil cylinder, with the gas cylinders of the sixth and seventh stages arranged vertically on top. The arrangement is kept as compact as possible, so as to obtain a short column of oil. An oil pipe of ample size runs from both sides of the primary oil piston to below each of the secondary pistons, in such a way that the motion of the primary system is transmitted direct to the secondary pistons by means of hydraulic columns. Unavoidable loss of oil through leakage, blowing off of valves, or the limitation of the stroke, as mentioned below, would shorten the column and thereby tend to make transmission of movement inexact; such loss is compensated automatically by the supplementary feeder pump after each stroke. Each side of the transmission column is rendered safe from excessive stresses by the provision of safety valves. Should a plunger stick for some reason or other no damage will be caused to the machine, as would otherwise inevitably be the case with a purely mechanical means of operation, as the appropriate safety valve would open and the oil-pressure column would collapse; in other words, after the plunger concerned has stopped working, the machine can run on safely for some time, i.e. until the attendant has been able to stop it.

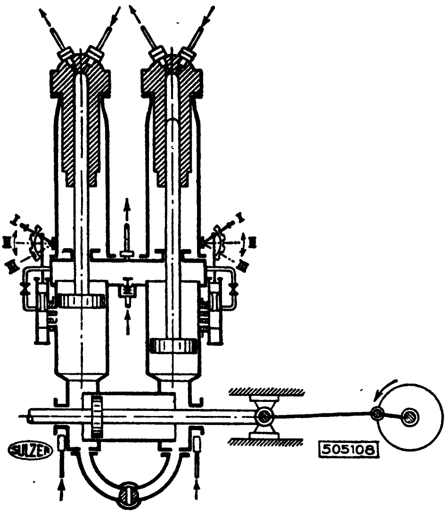


FIG. 35.—Section through hydraulic drive of sixth and seventh stages of Sulzer 1000 atm. compressor.

The plungers are connected by means of flanged couplings to the piston-rods of the secondary oil pistons, whilst the gas cylinders themselves are placed into the frame from above; dismounting these cylinders is therefore very easy, as the cylinders with plungers and glands may be lifted out from the top by a crane after undoing the coupling bolts and fixing bolts in the cylinder frame. In the same way, a replacement cylinder made ready previously can be fitted in, so that the duration of any interruption of operation as a result of changing plungers can be reduced to less than an hour.

The vertical arrangement of the cylinders of the hyper-stages, besides facilitating dismantling as mentioned above, also ensures the pistons remaining perfectly central during the whole stroke, upwards or downwards. The result of this is less wear on the packing, which usually remains good for 3000 hours' service, or more, without requiring the slightest attention.

The hyper-cylinders are made of specially tough Siemens-Martin steel, and are of the typical mushroom form, as will be recognised from the sectional drawings ; this form corresponds approximately to a body of uniform strength. The mushroom head contains the valves, and the great thickness of the walls provided there is necessary owing to the weakening of the material by the radial arrangement of the valve borings. A cooling jacket is not considered necessary, but it can be easily fitted if required by special circumstances. On the other hand, the plungers are intensively cooled by water, which is conducted through a central boring and run in and out by means of pipes in the usual way. Cooling is augmented by an ample circulation of oil in the front gland, which is constructed in such a way that the plunger moves in a continuous bath of cold oil.

The stuffing box (Fig. 36) is fitted with flexible throat elements (four for the sixth stage, and five for the seventh). The elements are located singly in steel chambers, and their angles, which vary from element to element, are arranged so that the drop in pressure inside the packing itself gives as far as possible an even tightening up of all the elements. There is a bronze guide bush above the throat elements, which guides the plunger, keeps all large impurities from the elements, and also serves to take up a portion of the reduction of pressure. The front gland is situated lowest of all ; it likewise contains flexible packing elements, and serves mainly as an oil scraper, as well as for cooling the plunger by means of a circulation of cool oil. Lubrication of the actual packing is effected at three different places, which are connected to corresponding delivery pistons of the high-pressure oil pump, and the arrangement is such that the oil supply to each individual lubrication point can be accurately controlled at all times. It will be readily understood that good lubrication of the glands is extremely important, because of the extremely high pressures which come into question.

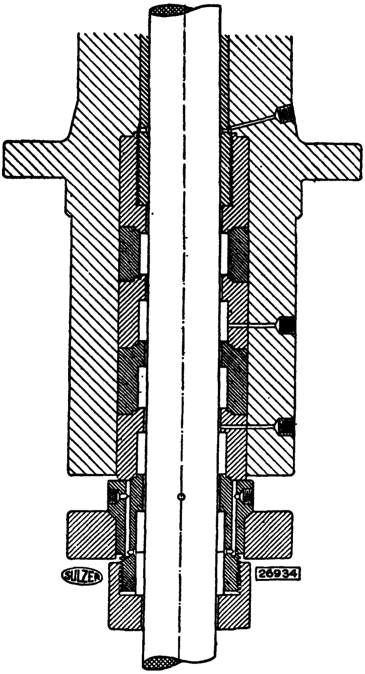


FIG. 36.—Stuffing box of Sulzer 1000 atm. compressor.

The main characteristic of the valves for the highest pressures is the valve head without a guide (Fig. 37). With the Sulzer valve, the valve head hangs on the spring, and as long as the spring is free to move even an encrusted valve will act properly. The place of contact on the valve seating alters with each stroke, as the valve head operates with a dancing movement. As a result, on the one hand, mechanical impurities are automatically removed from the seating surface, and, on the other hand, the valve seating does not wear the valve head, which means that the valve is preserved much better. The stroke of the valve can be adjusted as required by suitable formation of the valve stop, which, at the same time, serves as a spring guide.

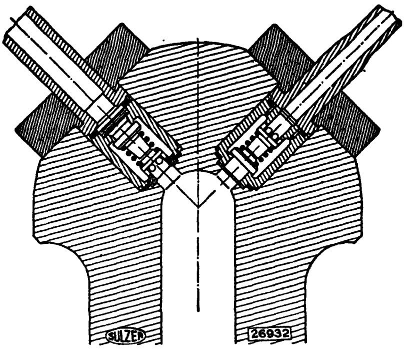


Fig. 37. — High-pressure delivery valves of Sulzer 1000 atm. compressor.

A further characteristic of the Sulzer hyper-compressor is the limitation of stroke of the plungers for the sixth and seventh stages (Fig. 38); this permits of the stroke of the plunger being adjusted, which is technically equivalent to regulation by altering the clearance. If the limitation of stroke is shifted downwards, the plunger at the top of its stroke is lower, and the cylinder affected thereby operates with an increased clearance. The reverse holds good in the case where adjustment is set for a greater stroke.

For altering the stroke, the secondary oil cylinder has a number of oil outlet channels which are opened or closed by the secondary piston; these channels discharge into an oil reservoir through a slide valve, which can be adjusted by hand. The number of channels opened depends upon the setting of this valve, and the piston, in its movement upwards, comes to a stop as soon as the first open channel is reached.

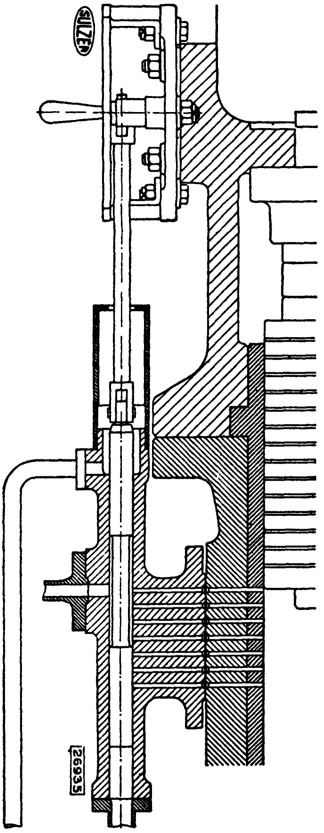


Fig. 38.—Stroke adjustment of Sulzer 1000 atm. compressor.

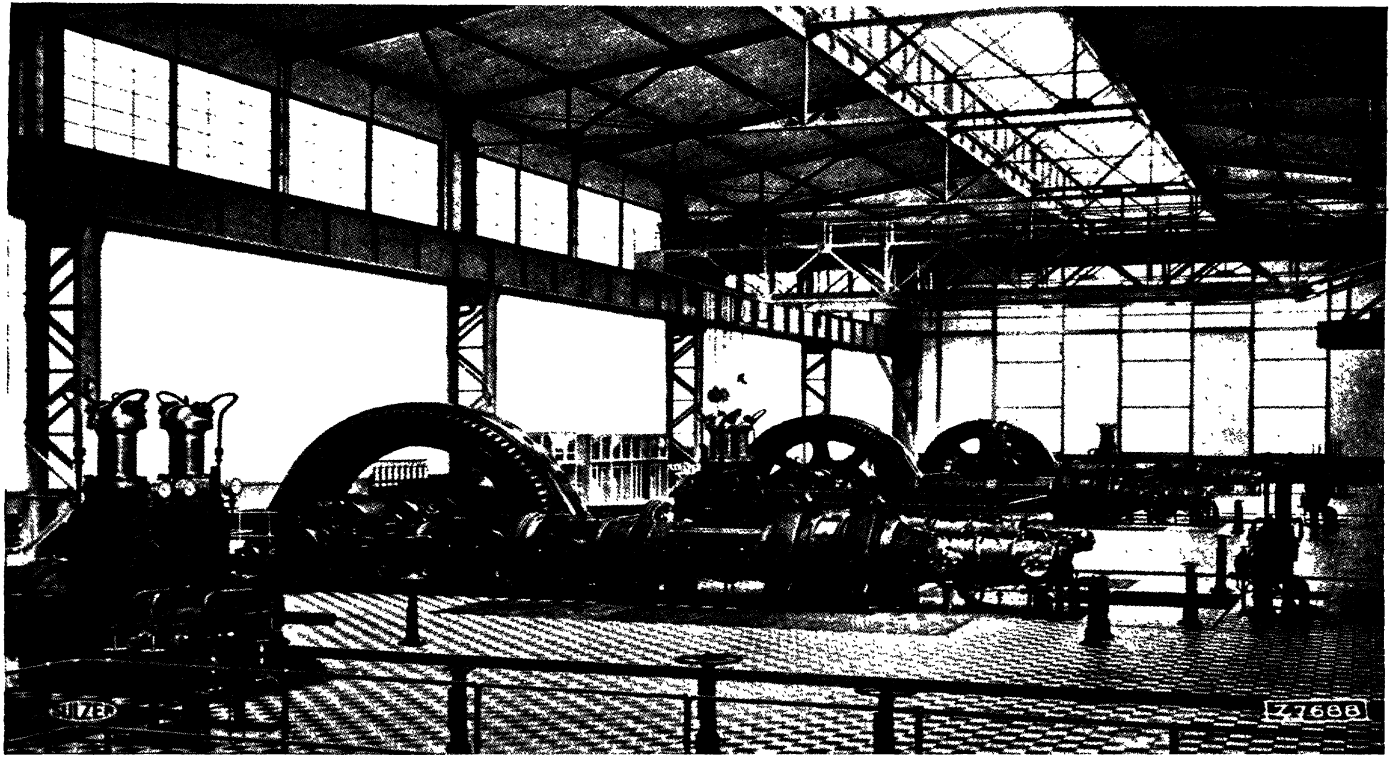


FIG. 39.—Three Sulzer 1000 atm. hyper-compressors in an ammonia works using the Claude system.

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The two hyper-compressors at Bethune have been in service since the beginning of 1930. The pressure of 1000 atms. was attained without trouble by both machines, so that they could at once be put in continuous service at full load. Measurements taken at the official trials showed that each compressor handled 4534 cu. metres of mixed gases per hour (reduced to 15° C. and 760 mm. Hg), the net power required, as measured at the shaft, being 2056 B.H.P.

A photograph of an installation of Sulzer hyper-compressors is seen in Fig. 39. Each of the compressors has a suction volume of 2650 cu. ft. per minute and the power required is 2000 h.p.

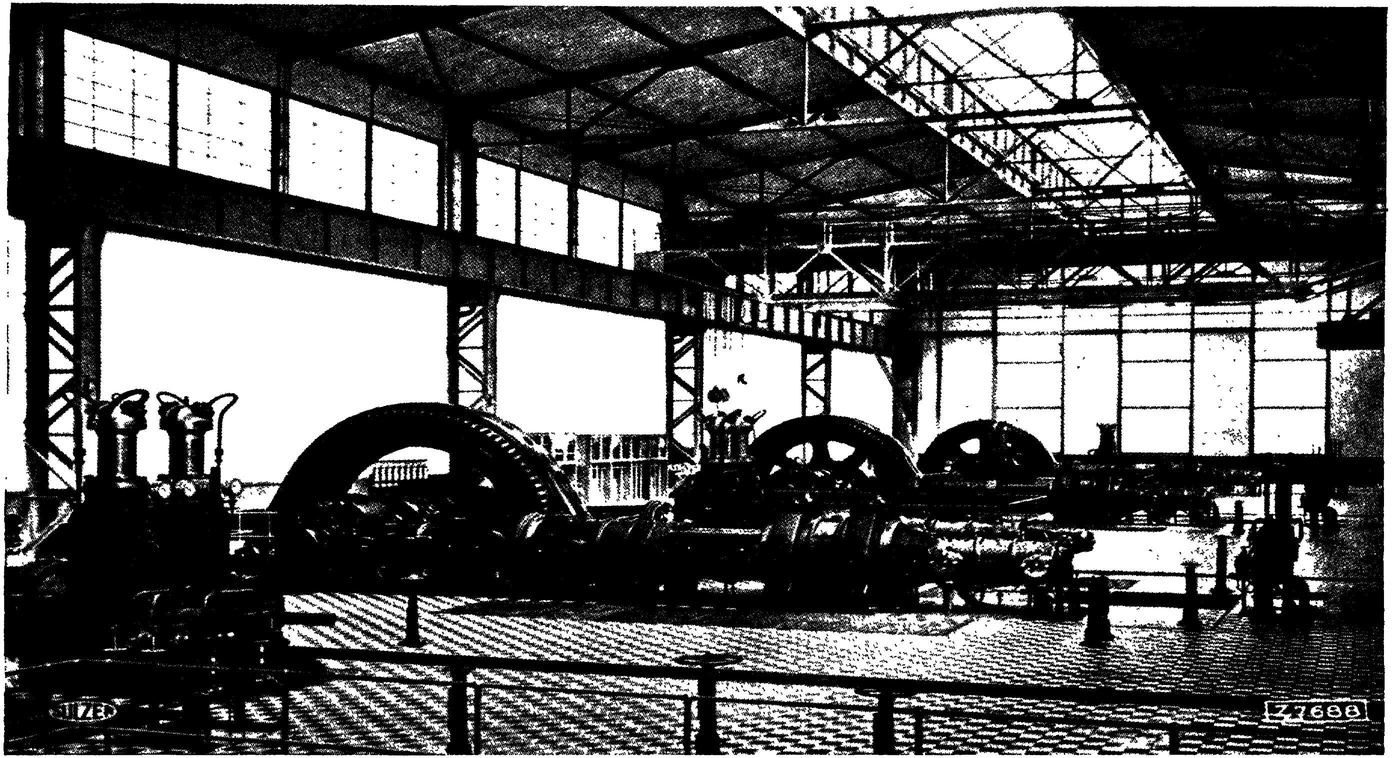
Amsler 4000 *atm. Compressor.*

Probably the highest pressure ever handled in a reciprocating power-driven gas compressor is 4000 atms., and a machine for this purpose was recently built by Alfred G. Amsler & Co., of Schaffhouse, Switzerland, for L'Institut de Chimie de l'Ecole Polytechnique de Zürich.

It is shown in Figs. 40, 41 and 42. It is a four-stage machine, and the first stage compresses to 6 atms., the second to 37 atms., the third to 230 atms., and the fourth compresses to the final pressure. The four cylinders are single acting and placed vertically with their lower ends open to the atmosphere. They are disposed in pairs, one over the other ; on the one side are the first and third stage cylinders, and on the other the second and fourth stages. It will be seen that the machine is belt-driven, and the two cranks for the two connecting rods are driven by gearing, and so arranged that as one pair of pistons is on the compression stroke the other pair is on the suction stroke.

The compressor pistons are not packed by hydraulic leathers or similar devices. The seal between the piston and cylinder is made in each case by means of oil or other viscous liquid, which fills an annular chamber surrounding the piston, in the portion of the cylinder serving as a guide for the motion. The pistons are ground and lapped and fitted exactly each to its cylinder, so that the pistons slide freely therein. The oil in the annular chambers prevents, on the one hand, the loss of gas between the piston and the cylinder wall, and, on the other hand, it efficiently lubricates the pistons so that there is a minimum of friction. The cylinders and pistons are made from the same material, and their mass is so large compared with the mass of gas passing that they heat up equally and uniformly without risk of jamming or seizing of the pistons. The considerable weight of the cylinders and pistons is such that water-cooling of cylinders or intercooling of gas between each stage is quite unnecessary.

In all the pipe lines between the various stages, pressure gauges



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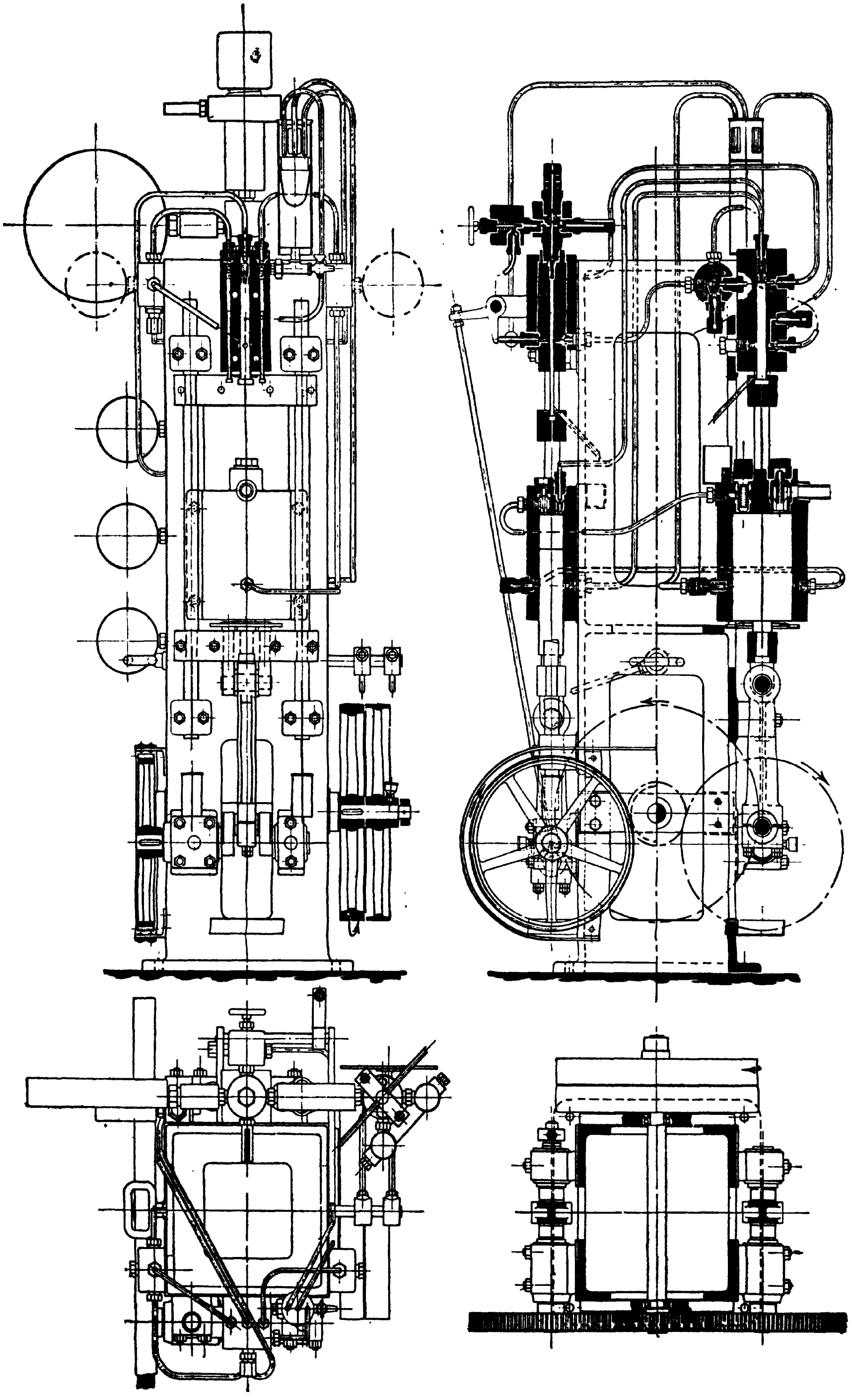

FIG. 40.—Section through Amsler 4000 atm. gas compressor.

are inserted so that the work done by each cylinder can be watched very carefully, and any trouble rectified at once. Safety valves are fitted to prevent overpressure developing in the various stages (due to valve leakage) from a higher stage.

On the top of the fourth stage cylinder is fitted a manifold, to which is screwed a receiver, closed at the top end by a cap and in which the compressed gas is delivered. The internal capacity of the receiver and the construction of the closure allow the introduction into the interior of a body or substance contained in a test tube, in order to expose it to the action of the highly compressed gas, with a view to the study of possible chemical reaction. The interior of this receiver may also be closed by a plug with two insulated electrical leads fitted through it, in order that the interior of the receiver may be heated by an electrical resistance placed inside it. A thermo-couple may also be fitted through the plug to permit measurement of temperatures inside the chamber during a reaction.

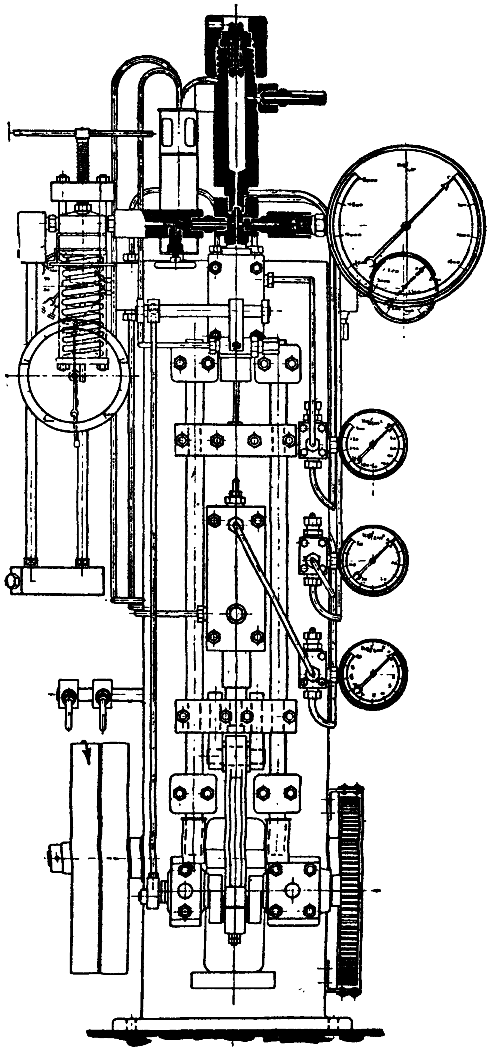

Fig. 41.—Side elevation of Amsler 4000 atm. gas compressor.

The receiver is made in special steel, with a wall thickness such that there is no permanent deformation under an internal gas pressure of 5000 atms. To avoid all danger of an internal explosion, this receiver is furnished with a safety branch, formed of a thick walled tube, closed at its free end, and fitted to the receiver by a screw connection, as shown in Fig. 41, and with which it is in communication. The thickness of the tube is weakened at one part by a longitudinal slot as shown, which yields when the internal pressure passes the admissible limit. The length of this receiver is 24 cm., and the diameter 4 cm., which corresponds to an internal volume of approximately 300 $cm.^3$.

The manifold which carries the receiver also carries a Bourdon pressure gauge graduated to 5000 atms., and shielded by a little check valve from sudden overpressure in the receiver. The manifold is also fitted with valves for the discharge of the compressed gas in the receiver, and to seal the receiver from the compressor final delivery. A special precision manometer may also be fitted to this manifold to measure the exact pressure to 5000 atms. It comprises a piston of small diameter, which under the pressure compresses a large helical spring, the deflection of which is indicated by a pointer on a quadrant. The measuring piston of the precision manometer is, like the compressor pistons, maintained gas-tight by an oil chamber around it.

In place of the reaction vessel already described, other attachments may be made to the manifold at the head of the fourth compressor stage. For example, a pipe connection carrying the compressed gas to another receiver, or a tube closed at its extremity and in the bore of which is cemented a glass capillary tube open at its lower end. The metallic shield tube is perforated transversely in several places, in such a manner as to permit observation of the inner glass capillary. This arrangement permits the observer to determine the instant when the highly compressed gas changes its physical state and becomes liquid. At this instant drops of liquid are deposited on the walls of the internal capillary tube and these are quite readily seen through the transverse observation holes.

The oil chambers surrounding all the pistons of the compressors are constantly fed with oil by two little pressure pumps. At each stroke of the pistons of the compressor these pumps draw in oil from the reservoir placed on top of the machine, and deliver it to the annular chambers of the different cylinders ; any excess of oil is returned to the oil reservoir by relief valves fitted to each annular chamber. The loading of the springs of the relief valves is such that the pressure of the oil held by each chamber is in proportion to the pressure of the gas in the cylinder, so as to avoid the entry of oil into the compression space. The annular oil chamber surrounding the fourth stage is (in order to proportion the delivery of the oil to the very small volume of the cylinder) fitted with an oil-pressure supply valve mechanically operated by levers and eccentric keyed to the crankshaft. The oil pressure, which in this case may rise to 4000 atms., is relieved at the correct moment by the opening of the relief

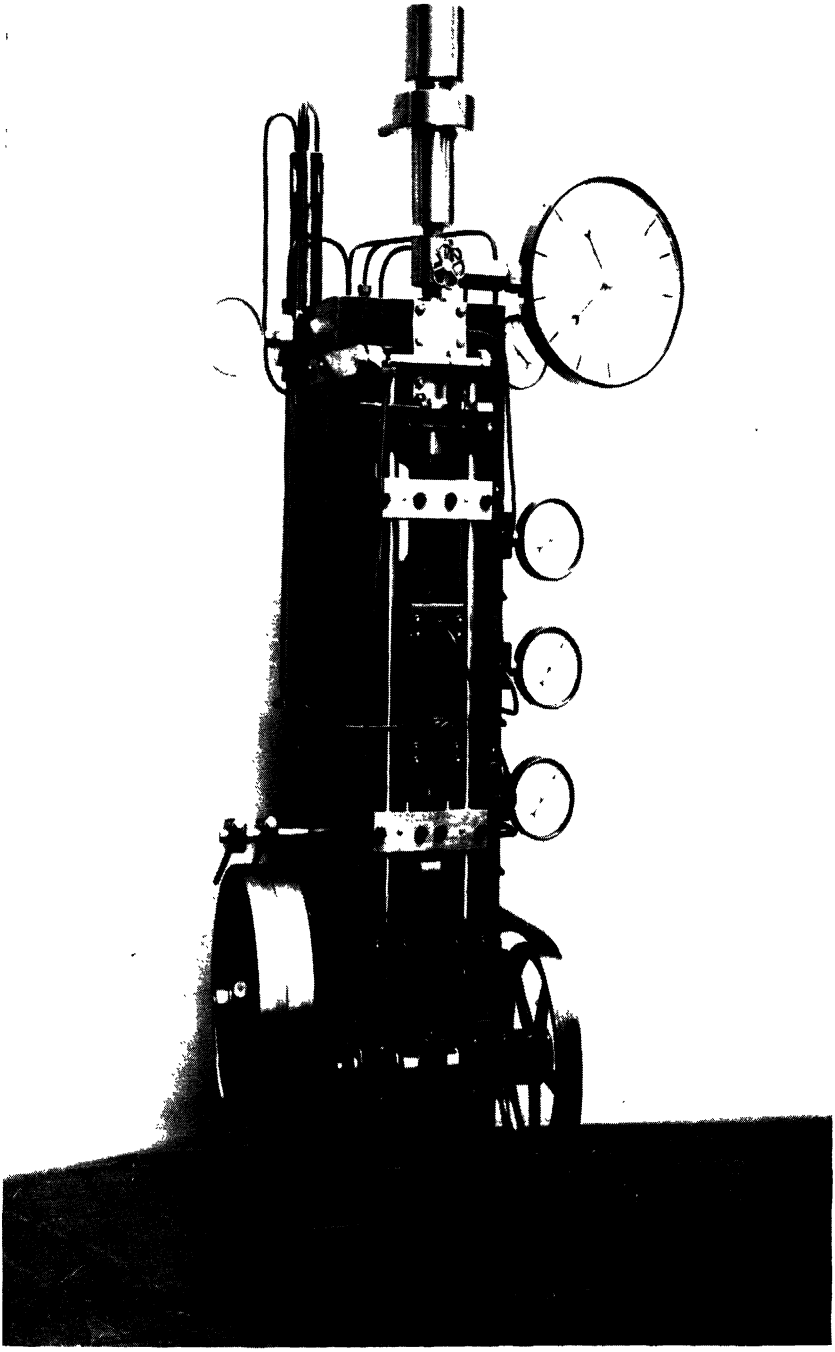

FIG. 42.—Amsler 4000 atm. gas compressor.

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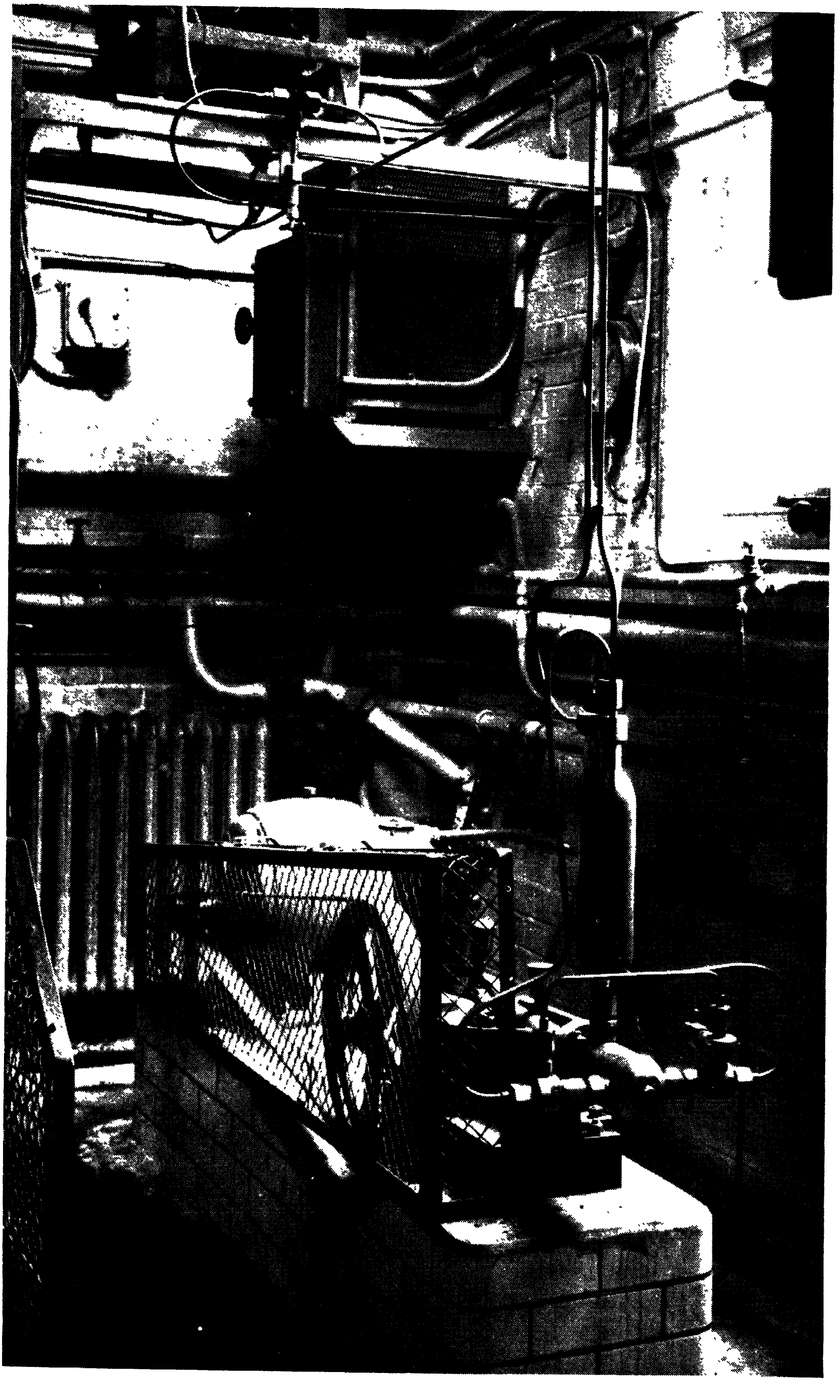

FIG. 44.—Hofer single acting circulating pump.

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valve by the motion work controlled by the operating levers ; this point is clear from the drawing.

The oil serving to ensure tightness between the piston and cylinder walls penetrates slightly into the compression space of the cylinders. The best seal liquid is, of course, highly viscous oil. In certain cases, however, one may be forced to replace it by another viscous liquid, for example, glycerine or molasses, when, with the compressed gas, heavy lubricating oil might form an explosive mixture, as, for example, in the case of oxygen. When compressing atmospheric air, it is possible to compress as high as 2000 atms. without danger, even when using lubricating oil. At 2500 atms., however, little explosions occur, which, although not sufficiently violent to damage the machine, might blow the safety tube. Naturally, with gas mixtures rich in oxygen, this trouble becomes more serious.

If the machine were driven at uniform speed the pressure in the fourth stage and receiver would rise very rapidly indeed when the critical pressure was reached and liquid formed in quantity. Hence, the machine is driven at widely varying speeds, with a very " weak " drive so that it can be stopped at the "psychological moment." Belt-drive is recommended so that the operator can throw this over to the loose pulley when occasion demands prompt stoppage of the machine.

The compressor can deal with 1·2 litres (·042 cu. ft.) of free gas per revolution. If, therefore, the machine operates at 10 useful strokes per minute, the capacity is 720 litres (25 cu. ft.) of free gas per hour. In the early stages of compression, say to 1000 atms. or so, the speed of the machine may be increased considerably over this figure. A photograph of the machine is seen in Fig. 42.

High-Pressure Gas Circulating Pumps.

In all high-pressure gas catalytic plants of a circulatory character, i.e. where the gas stream is continuously circulated over the catalyst mass, a high-pressure gas circulating pump is essential. In the majority of cases this is merely a single-stage compressor, and the only work done by it is to overcome the friction of the system.

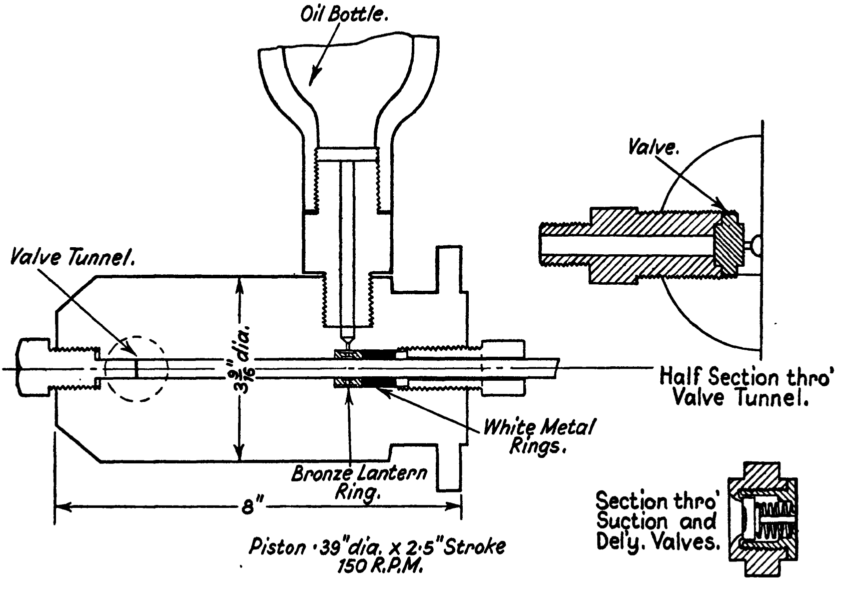
Several types will now be described of both laboratory and works interest.

Hofer Gas Circulating Pumps.

In addition to compressors Andreas Hofer also builds a series of high-pressure gas circulating pumps, such as are required for experimental work in connection with catalytic syntheses employing gases which are continuously circulated at high pressure over a catalyst. The capacities and working pressures of these Hofer circulating pumps range from the single acting No. 1 model for pressures of 200 atms. and volume displacement of 24 litres per hour, to the double acting No. 8 model for pressures of 1000 atms. and 1000 litres per hour.

A small Hofer single acting circulating pump is seen in Figs. 43 and 44. This has a capacity of 40 litres (1·4 cu. ft.) per hour, and is suitable for working pressures of 300 atms. It has been in use for several years at the Chemical Research Laboratory in conjunction with the 1 in. converter catalytic circulatory plant which is described later in Chapter X.

This circulating pump has a piston diameter of 0·39 in., and a stroke of 2½ ins., and the speed is of the order of 150 r.p.m. At 300 atms., the power required to drive is about 0·8 h.p. A section of the cylinder is given in Fig. 43.


Oil Bottle.
Valve.
Valve Tunnel.
3⅜" dia.
Half Section thro' Valve Tunnel.
White Metal Rings.
Bronze Lantern Ring.
8"
Section thro' Suction and Del'y. Valves.
Piston ·39"dia. x 2·5"Stroke 150 R.P.M.

SECTION OF CYLINDER OF SMALL HIGH PRESSURE GAS CIRCULATING PUMP

FIG. 43.

The cylinder is of steel, and the piston, which is of the plunger type, is quite a sloppy fit in the cylinder. The piston is packed with a lantern type of stuffing box, as shown, and adjustment of the white metal packing rings is by the external gland nut.

The oil bottle is filled prior to an experiment in the plant with about 350 c.c. of oil, and the oil bottle is maintained at the same pressure as that in the plant. The pipework to effect this is clearly seen in the photograph. Adjustment of the rate of flow of the gas round the circulatory plant is by a by-pass valve which opens a connection between the delivery and inlet sides of the pump. This valve is shown in the photograph.

The suction and delivery valves of this machine are exactly as those previously described for the Hofer compressors, but an assembly drawing of these valves is given here for reference purposes.

An outline drawing of a larger double acting Hofer circulating pump is shown in Fig. 45. This machine is suitable for a throughput of 1000 litres per hour (35 cu. ft.) at 200 atms. The speed of the machine is 150 r.p.m., and the power required is about 2½ h.p.

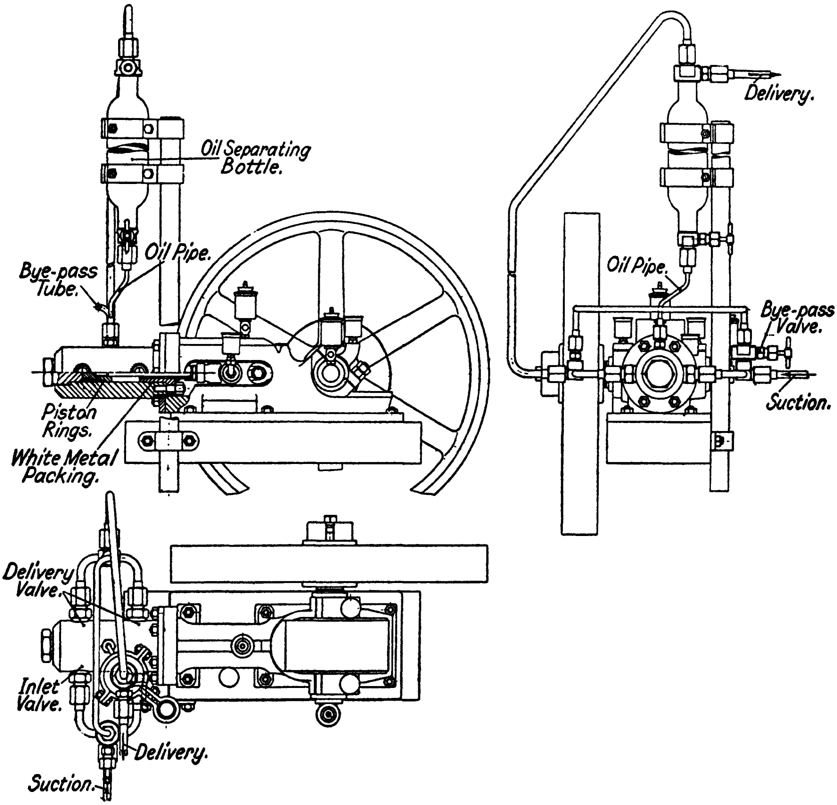


FIG. 45.—Hofer double acting high-pressure gas circulating pump.

It will be noted that the piston, which is of cast iron, is fitted with cast-iron carrier rings and piston rings, which are retained by a junk ring.

The cylinder is lubricated by means of a pipe led from the oil bottle, and a valve is interposed to regulate the flow of oil to the cylinder. The piston-rod stuffing box is again packed with white metal rings. As in the case of the single acting pump just described, there is a by-pass valve to regulate the speed of gas circulation round the apparatus.

It will be noted that these circulating pump cylinders are not water-cooled. In experimental practice but little actual compression work is done by these machines. At pressures of the order of 200 atms. the pressure on the suction side of the circulating plant will be of the order of 198 atms., and on the pressure side about 202 atms. or so. Hence, there is but little heat of compression to dissipate, and this is taken care of by the pipework. Naturally, the amount of compression depends upon the resistance of the system to free flow of gas, but in well designed experimental plants this is almost negligible.

Brotherhood Large H.P. Gas Circulating Pump.

An example of a large gas circulating pump is shown in Figs. 46 and 47. The suction pressure is 228 atms., and the delivery pressure 250 atms., i.e. the conditions required for the circulation of gas in a process such as the Haber-Bosch for the synthesis of ammonia. This machine is of the 3-cylinder, double acting, 3-crank type (all cylinders are exactly similar) and capable of dealing with 200,000 cu. metres (over 7,000,000 cu. ft.) of free gas per hour. (Assuming Boyle's law, the actual machine displacement is therefore 7,000,000 ÷ 228, or just over 300,000 cu. ft. per hour.) The piston is 11 ins. diameter, the stroke 18 ins., and the speed is 120 r.p.m. The crank case is of the enclosed pattern with forced lubrication to all bearings, and the cylinders are mounted on an entablature which is held to the crank case by eight hollow steel pillars and through bolts, in accordance with Brotherhood's standard practice. Each piston is fitted with sprung-on piston rings, and is lubricated by two pressure-fed oil ports (seen at the centre of the cylinder in the end elevation). The piston-rod is carried right through the cylinder, so that the piston is running under more or less balanced pressure conditions. The piston-rod and the tail rod are both fitted with metallic packings, and lantern rings are fed with oil at appropriate pressure by a mechanically driven oil pump.

The cylinders, covers, valve boxes, etc., are of forged steel throughout.

The valves are of the spring loaded thimble poppet type, and there are eight suction and eight delivery valves per cylinder. These are mounted in valve boxes in groups of four. The valves are all interchangeable, and the ports to the cylinders are therefore taken from beneath and above the boxes, as shown in the enlarged drawing. The overall height of the machine is 24 ft., and the power required to drive is 1500 h.p.

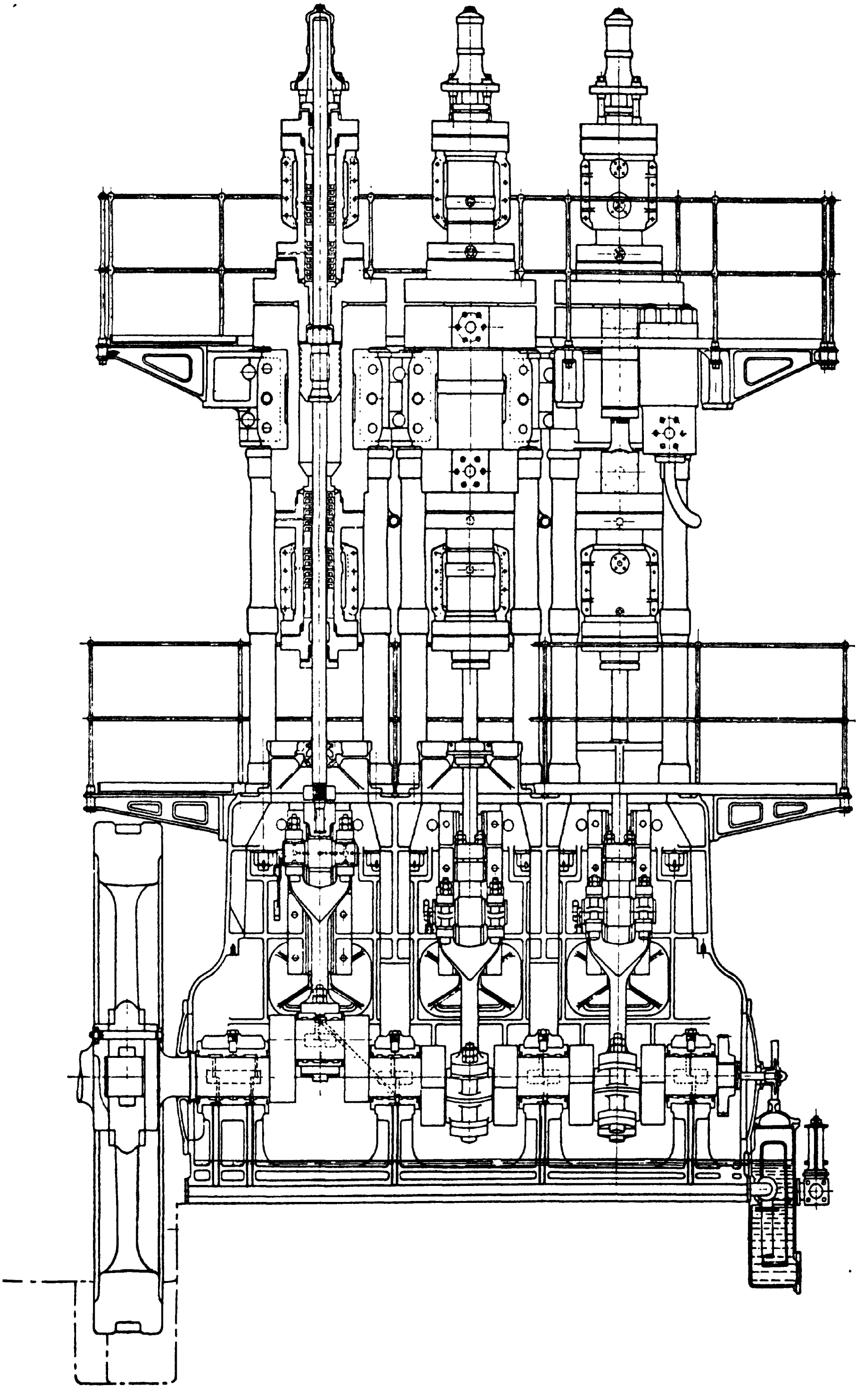


FIG. 46.—Brotherhood high-pressure gas circulating pump.

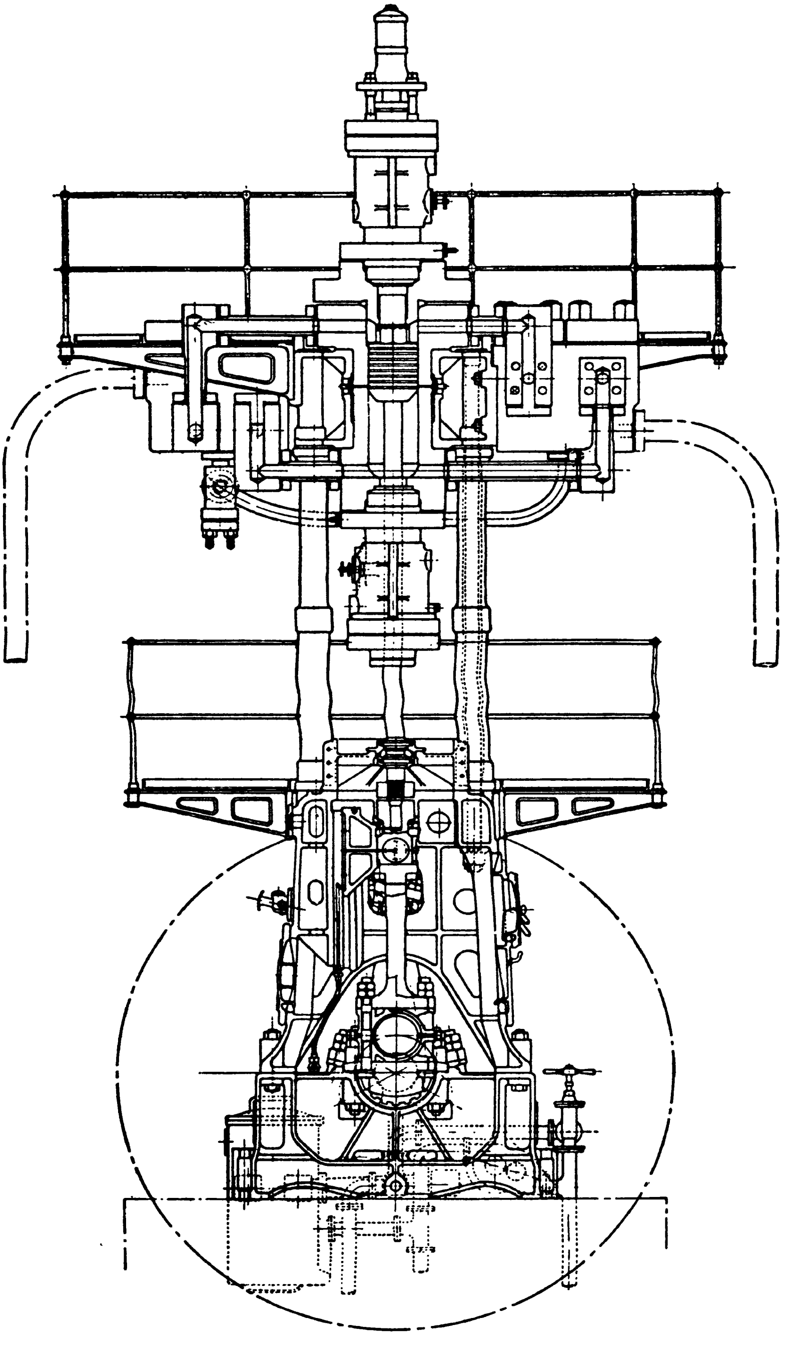


Fig. 47.—Brotherhood high-pressure gas circulating pump.

Sulzer 1000 *atm. Gas Circulating Pump.*

A quite different type of high-pressure gas circulating pump, built by Sulzer for 1000 atms. pressure, is shown in Figs. 48, 49 and 50.

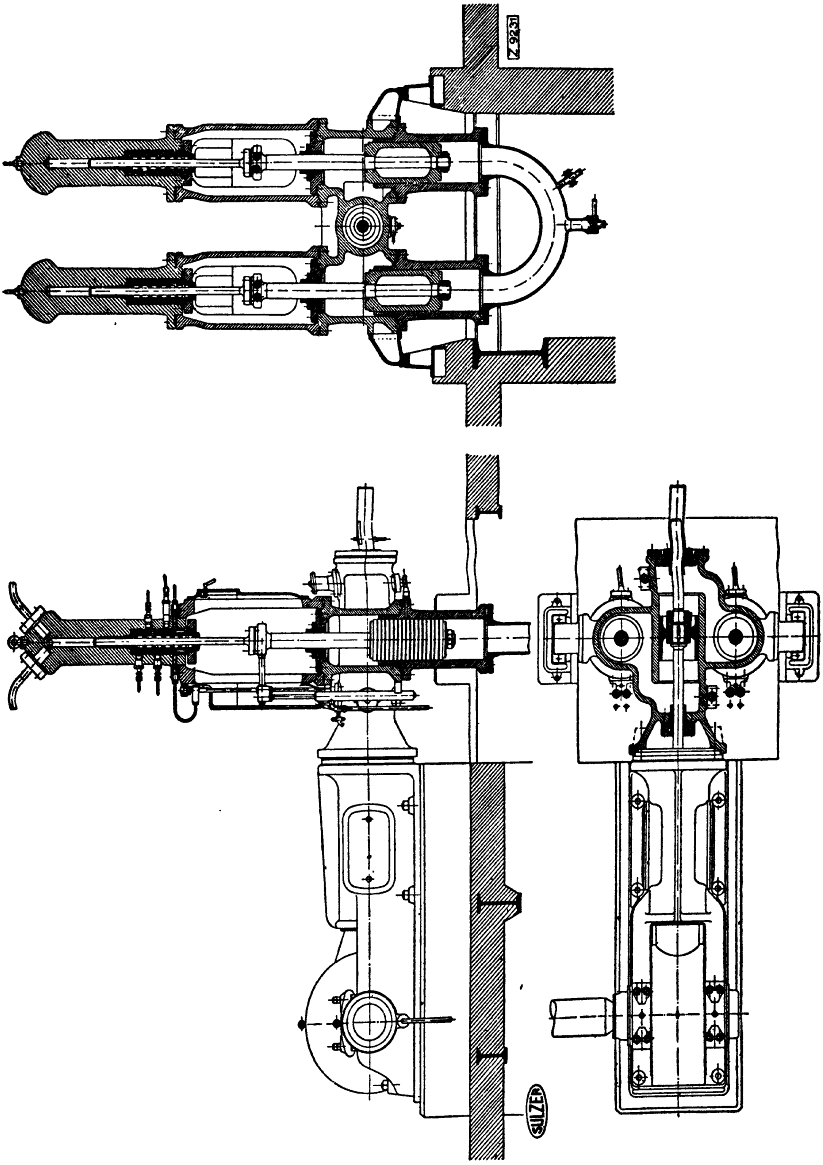


Fig. 48.—Sections through Sulzer 1000 atm. gas circulating pump.

As mentioned in Chapter I., when manufacturing synthetic ammonia according to the Claude process, the gas enters the synthetic apparatus at a pressure of 1000 atms. This process with one catalyst tube gives a yield of ammonia of about 25 per cent., so that with four tubes arranged in series, all but a comparatively insignificant amount of the gas coming from the compressor is converted into ammonia. Consequently the circulating pump, which is generally necessary for maintaining a regular circulation of the gas (in processes such as the Haber-Bosch) has up to the present not been adopted in the Claude process. The gas which was left over, issuing from the fourth catalyst tube still at a pressure of 850 atms., was allowed to expand down to 25 atms., and added to the fresh synthetic mixture in the coke oven gas treating apparatus. Of course, this method entailed a certain loss of energy, but this was considered to be compensated by the simplicity of the plant.

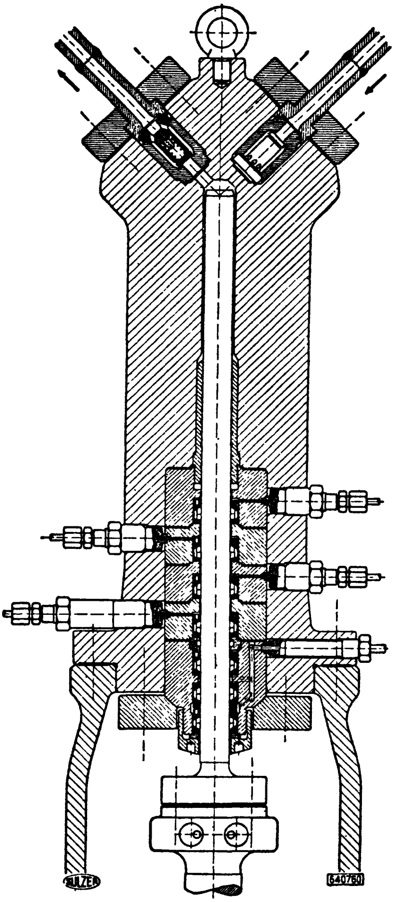


FIG. 49. — View of high-pressure piston packing of Sulzer 1000 atm. gas circulating pump.

In order to eliminate this loss, and thereby increase the efficiency of the Claude process, which was already high, the process has lately been carried out in a somewhat different manner. The gas left over from all the catalyst tubes is collected by means of a special circulating pump and compressed from 850 up to 1050 atms., and then converted as far as possible into ammonia in another catalyst tube.

A high-pressure gas circulating pump for carrying out this new process was recently built by Sulzer Brothers. The design of the pump is based on that of the Sulzer hyper-compressor. As can be seen from Fig. 48, the pump has two single acting vertical cylinders, the pistons of which are worked hydraulically. This method of construction gives a very good distribution of pressure; in this respect it may be compared with that of double acting single-cylinder pumps.

The oil pistons for driving the two plungers are connected together by a U-shaped tube, through which the pressure on the two sides is

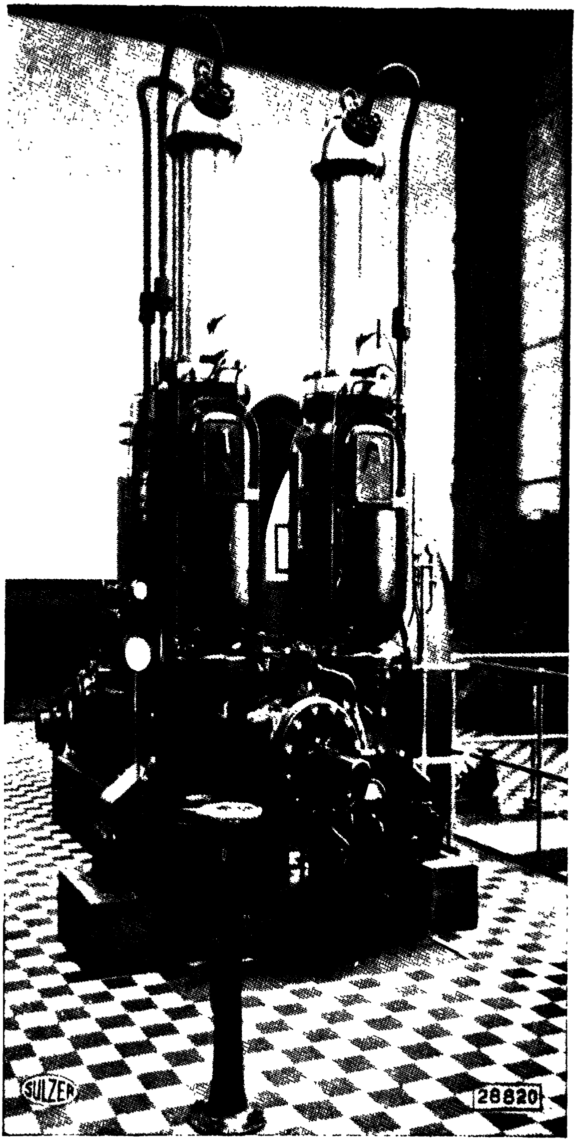


FIG. 50.—Sulzer 1000 atm. high-pressure gas circulating pump.

[*To face page* 81.

equalised. In consequence of this, the only effective power required for operating the plungers is that necessary for overcoming the difference in pressure between 850 and 1050 atms., so that the frame and the driving gear can be made lighter in correspondence to the lower stresses to which they are subject. The plungers are driven by oil columns, which transmit to them the motion of the horizontal primary pistons. The other constructional parts, stuffing boxes, valves, auxiliary pumps for the oil drive, safety devices, etc., were also taken over from the hyper-compressors. The oil delivered under pressure for cylinder lubrication, the sealing oil for the stuffing boxes and the make-up oil for the hydraulic drive, is supplied by an independent electrically driven pump. The electric motor driving this pump is electrically coupled with the motor driving the gas circulating pump, and is blocked by a relay in such a manner that the motor driving the gas circulating pump can only be switched in when the oil pump is working. A gearwheel oil pump, coupled to the main shaft, supplies lubricating oil under pressure to the mechanical parts, such as main bearings, cross-head bearings, slippers, etc. At the same time it supplies oil under pressure to the auxiliary pump of the hydraulic drive.

Fig. 50 shows a Sulzer circulating pump which has been in service in the nitrogen works of the Gewerkschaft Victor, Rauzel, since January, 1931. It was built for a suction volume of about 8000 cu. metres (or 280,000 cu. ft.) per hour at an initial pressure of 800 atms. and an end pressure of 1000 atms., the power required being 150 B.H.P. As a matter of fact, the pump is working to-day between pressures of 880 and 1100 atms.

The pump is driven by an electric motor through a belt with Lenix belt tightening device. Since the circulating pump has to take up all the gas left over from the catalyst tube, it is necessary to be able to regulate the speed within very wide limits, corresponding to the quantity of gas available at the moment.

It was decided to instal a three-phase motor with adjustable pole windings and regulation of the rotor through resistances. The construction of the motor and the necessary switch gear was undertaken by the Bergmann Elektrizitätswerke, A.G. The stipulated output was 145 kw. at 1465 revs. per min., and 100 kw. at 980 revs. per min. The torque is the same at both speeds. The supply is 380 volts, 50 periods. The motor was provided with two stator windings and two rotor windings (6-pole and 4-pole) in an air-tight casing with the slip rings outside. The starter is of the open type.

The speed of the gas circulating pump has to be regulated between 125 and 32 revs. per min.; it is, therefore, necessary for the speed of the motor also to be adjustable down to 25 per cent. of its maximum. With the 4-pole winding, the motor with adjustable pole windings and resistances in the rotor circuit can be regulated between 125 revs. per min. and 86 revs. per min. For the 6-pole winding, the regulation available is from 86 to 32 revs. per min. Since, however, completely electric regulation of the three-phase motor could only be obtained by means of very large resistances, and then also would be rather unreliable, a speed reduction gear with the ratio of 1 : 2 was fitted. The range of regulation was divided up in such a way that, when driving direct with the 6-pole winding the speed could be regulated down to $62\frac{1}{2}$ revs. per min., i.e. to 50 per cent. of the maximum. For obtaining lower speeds, the motor must work through the reduction gear. The motor is therefore regulated in two groups with 4-pole and 6-pole windings. The groups themselves are sub-divided into various stages, the 4-pole into twelve stages and the 6-pole into six. The gradual changes in speed thus made possible are sufficient for working the gas circulating pump in compliance with the different conditions arising in service.

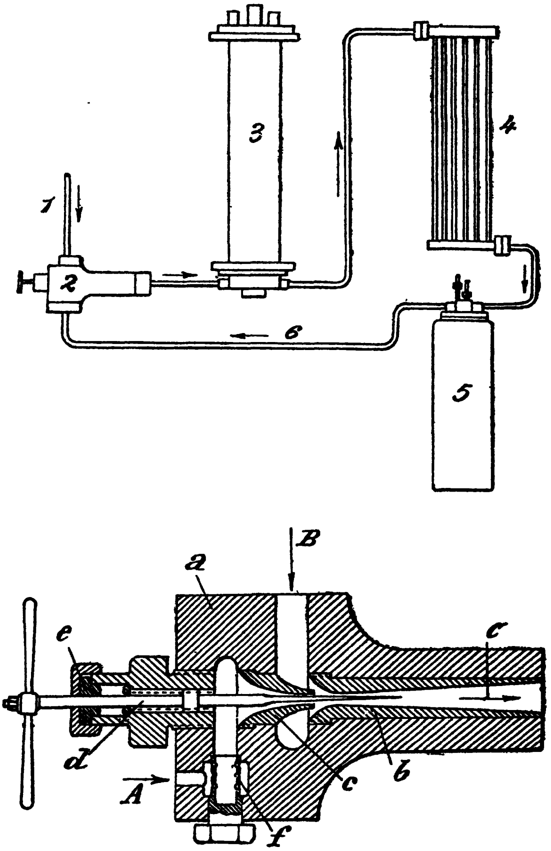


FIG. 51.—Casale injector type circulating device for high-pressure gas.

Casale Injector Type Circulating Device.

To avoid the contamination of the circulatory gases in catalytic plants with lubricating oil used in reciprocating circulating pumps, Casale has developed an injector type of circulatory device (E.P. 221956 of 1923).

The circulation of the gases in an ammonia synthesis plant is effected by using the driving force of the higher pressure of the fresh gas introduced into the system. As shown in the drawing (Fig. 51), the fresh gases are forced into the injector through the opening A at a pressure of 50-100 atms. greater than the pressure of the uncombined gases entering the injector from the ammonia separator by the opening B and the velocity of the circulation is adjustable by the needle *d*.

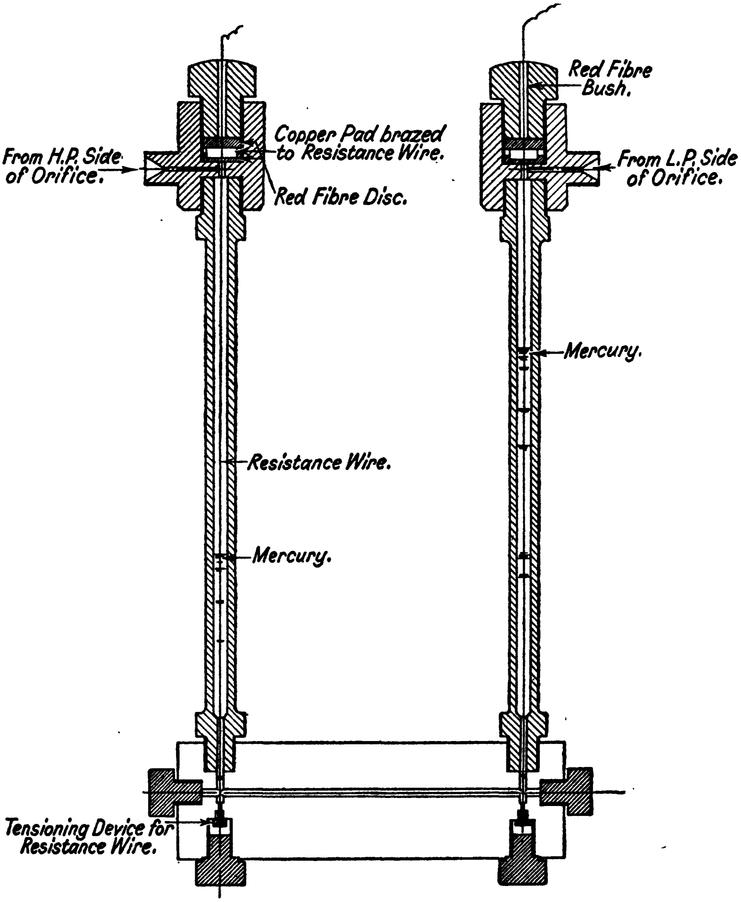

Red Fibre Bush.
Copper Pad brazed to Resistance Wire.
From H.P. Side of Orifice.
Red Fibre Disc.
From L.P. Side of Orifice.
Mercury.
Resistance Wire.
Mercury.
Tensioning Device for Resistance Wire.

FIG. 52.—U-tube for high-pressure gas orifice meter.

Methods for Measuring the Rate of Flow of High-Pressure Gas.

In high-pressure circulatory catalytic plants, it is, of course, important to know the rate of gas circulation over the catalyst mass. Perhaps the simplest method for this purpose (and one which is applicable to both small and large plants) is a meter of the orifice type, in which the difference in pressure at each side of an orifice plate is measured by means of a U-tube manometer. Fig. 52 shows a standard type of such meter in which mercury is used as the fluid. The position of the mercury in the arms of the tube is found from the resistance of the resistance wire placed as shown.

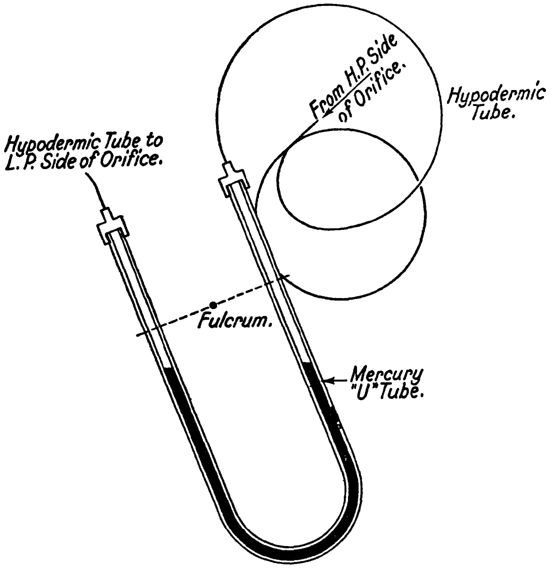

From H.P. Side of Orifice.
Hypodermic Tube.
Hypodermic Tube to L.P. Side of Orifice.
Fulcrum.
Mercury "U" Tube.

FIG. 53.—Swinging U-tube manometer for orifice meter.

The above design is only suitable for use with clean gases. Where difficulties are likely to arise in connection with the accurate measurement of resistance, due to contamination of the mercury, the relative position of the mercury level in the two arms may be found by mounting the U-tube on an axis, about which it is free to rotate, and connecting the two limbs to each side of the orifice plate by hypodermic tubing, which being quite flexible, imposes negligible restraint to the free movement of the U-tube. Fig. 53 will clarify this design.

Another variation of the above has been developed by Newitt and Sirkar (*Trans. Inst. Chem. Eng.*, 1931, 9, 63). They used an apparatus as shown in Fig. 54 for investigating the laws governing the flow of gases at high pressure in pipes. AA′ is the pipe, 18 ft.

long, whose resistance was measured. The actual pressure drop was measured over a 12 ft. length of pipe between the tees B and B′. The pressure difference between these two points B and B′ was measured by the differential manometer M, which is shown in greater detail in Fig. 55. The recording element of the manometer is a thin metal disc, rigidly held, whose movement is magnified by

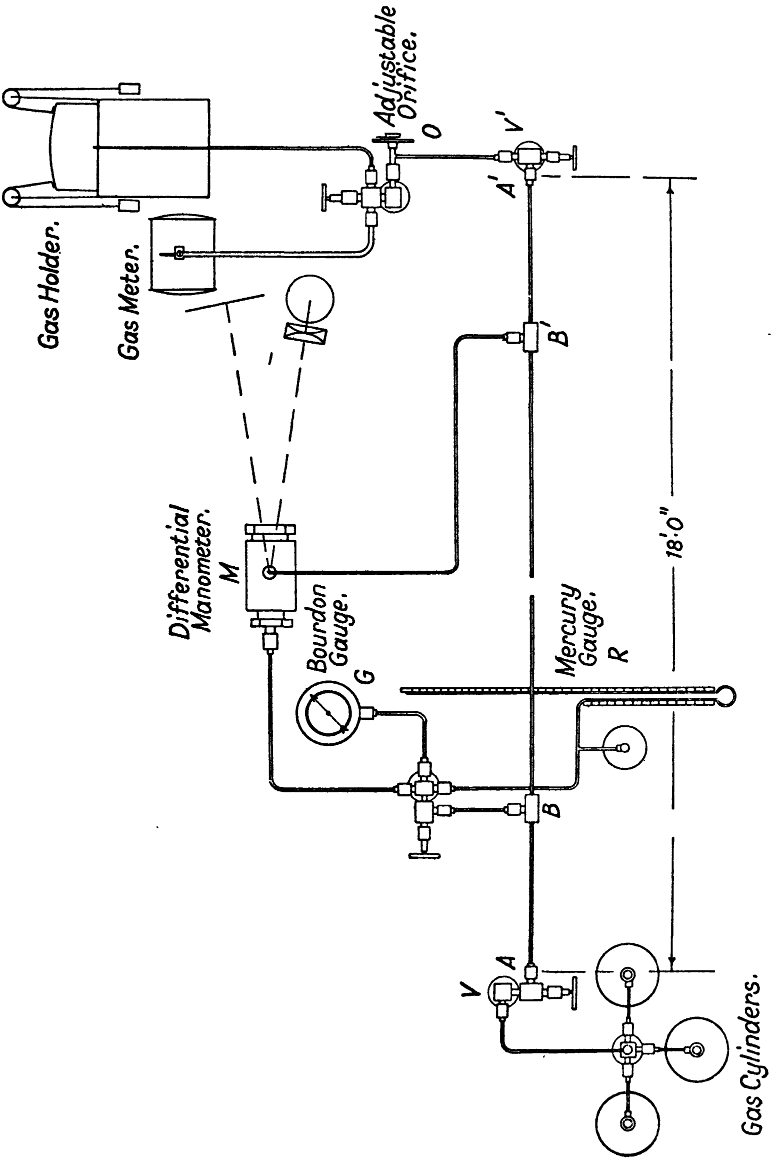


FIG. 54.

means of an optical lever. By employing a series of discs of graduated thicknesses, the sensitiveness of the instrument can be maintained constant over a wide range, and the authors found that by this method an accuracy of 1 per cent. was obtainable. Before and after each series of experiments the disc is calibrated against a mercury manometer R.

The recording element A (see Fig. 55) of the differential disc manometer is made of chrome vanadium steel having a narrow semi-circular corrugation concentric with the edge. It is rigidly clamped to the mild steel casing. Any movement of the disc due to a difference in the two pressures is transmitted to the concave mirror H by means of a light steel needle G and is magnified and indicated by the reflection of a beam of light passing through the conical quartz window W.

Since this window has to withstand the full gas pressure (say 400 atms.) care has to be taken provide it with the necessary support in the steel casing.

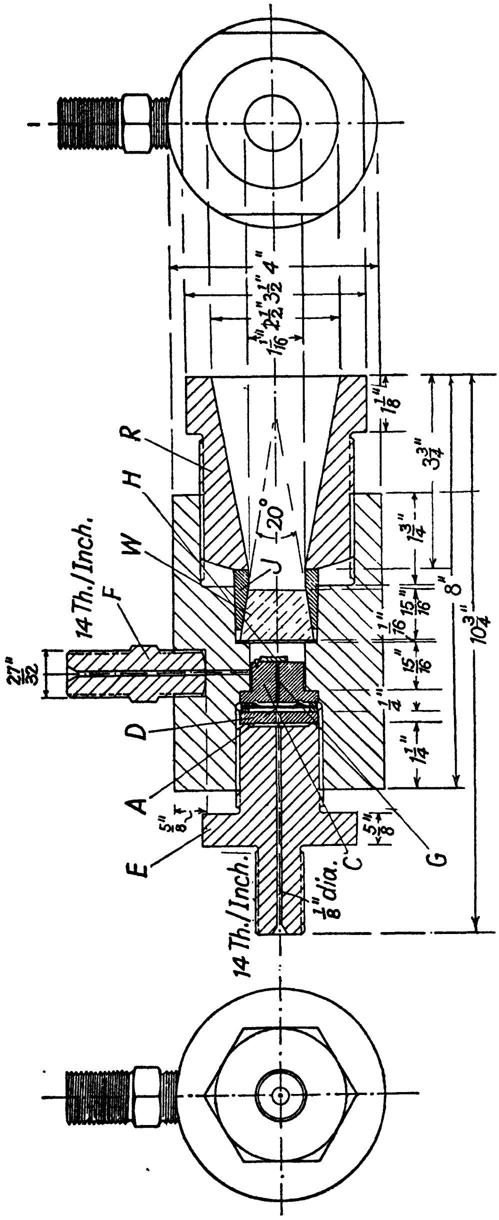


FIG. 55.

The authors calculated the thickness of disc required to produce a suitable deflection for a given pressure difference from the formula

$$t = \frac{Kpr^4}{ED},$$

where t = required thickness of disc,
D = deflection at the centre,
p = given pressure difference,
r = radius of disc,
E = Young's modulus,
and K = a constant having a value 1/6 for a disc rigidly clamped at the edges, when Poisson's ratio for the material is 1/3.

A quite different method for which I have recently obtained a provisional patent comprises a cylinder with a piston free to move in either direction, and moved to and fro by the gas stream in circulation round the system. The amount of gas passed by the meter depends upon the volume swept by the piston in moving from one end of the cylinder to the other. Suitable valve gear, electrically operated, causes the piston to reverse itself at each end of the stroke.

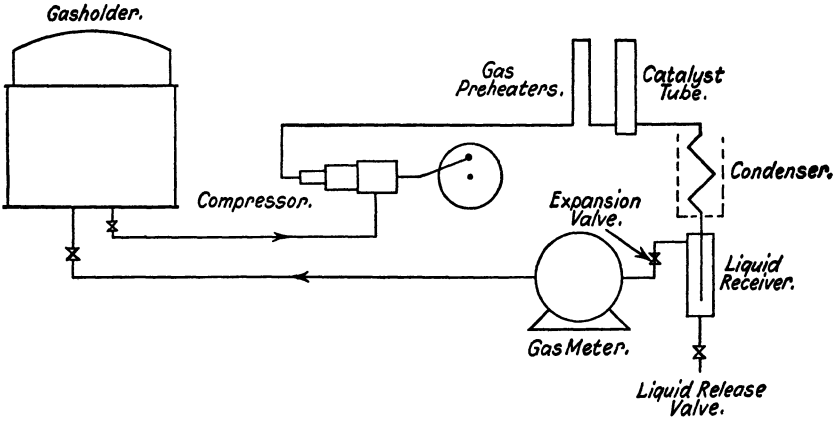


FIG. 56.—Flow-through method of measuring gas flow over a catalyst in a circulating plant.

It is often quite possible in many experimental plants to determine the rate of flow of the gas stream over a catalytic mass for given experimental conditions by means of a " flow-through " system, such as is illustrated in Fig. 56.

The reacting gases are compressed from a gasholder by a compressor and delivered to the catalytic plant, and there passed over the catalyst under desired experimental conditions. The gases are returned to the gasholder at low pressure through a commercial wet gas meter (such meters are accurate within 1 per cent.), whereby the rate of flow of the gas over the catalyst may be calculated. This method is frequently used to calibrate the orifice and other meters just described.

The gas meter may be replaced by another gasholder, into which the gases are delivered at low pressure after having passed through the catalytic plant. Volumetric calibration of the gasholder per unit height will give the gas speed when dealt with in regard to time.

CHAPTER III.

USE OF PRESSURE IN PREPARATION AND PURIFICATION OF INDUSTRIAL GASES.

A VERY interesting rôle is played by high pressure in modern industrial chemistry in the separation and purification of gases and gas mixtures. Perhaps the best-known application is that of the separation of the constituents of air.

The following is a description of the small laboratory air liquefying apparatus built by the British Oxygen Co. Ltd. of London, and is given as an introduction to the subject.

This apparatus depends upon a method by which a moderate amount of refrigeration, produced by the expansion of a gas, may be accumulated and intensified until it reaches the point at which the gas becomes liquid under atmospheric pressure. The method consists in directing all the expanded gas, immediately after its expansion, over coils which contain the compressed gas that is on its way to the expansion point. The cold developed by expansion in the first expanded gas is thus communicated to the on-coming compressed gas, which consequently expands from, and therefore to, a lower temperature than the preceding portion. It communicates in the same way its own intensified cold to the succeeding portion of compressed gas, which in its turn is made colder, both before and after expansion, than any that had gone before. This intensification of cooling goes on until the expansion temperature is far lower than it was at starting ; and the effect is so powerful that even the small amount of cooling due to the free expansion of gas through a throttle valve may be made to liquefy air without using other refrigerants.

The amount of refrigeration due to free expansion was ascertained by Joule and Thomson, and is in the first place proportional to the fall of pressure. Air at 0° C. is cooled 0·29 of a °C. for every atmosphere of pressure drop. This cooling, however, increases with the descent of the temperature from which expansion takes place, and the law is that it is inversely proportional to the square of the absolute temperature. Thus expansion of air from 4½ atms. to 1, and from a temperature of 0° C., i.e. 273° Absolute, gives about 1° of cooling in the air itself. But when the air expands from two-thirds of that absolute temperature, i.e. from — 91° C., the cooling for the same pressure drop is nine-fourths of 1°, or 2¼°.

The efficiency of the method depends upon the arrangement and construction of the coils and chamber forming the interchanger in which the expanded gas takes up heat from the compressed gas. To make this action as perfect as possible, the conditions required are : to have a large surface of exposure between the compressed and expanded gases ; to have little thickness of material between them, and that little of high conductivity ; to have both compressed and expanded gas in small masses in close contact with the conducting material ; to have the total volume of the interchanger small so as to expose little surface for the entrance of external heat ; and to have the total mass of coils and interchanger, which have to be cooled down with the gas, small and of little specific heat. These are all thermal advantages.

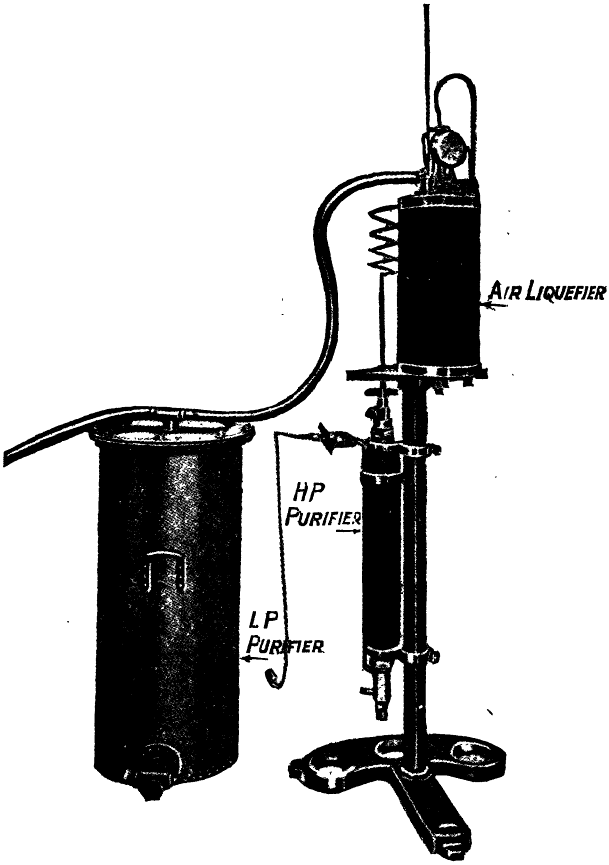
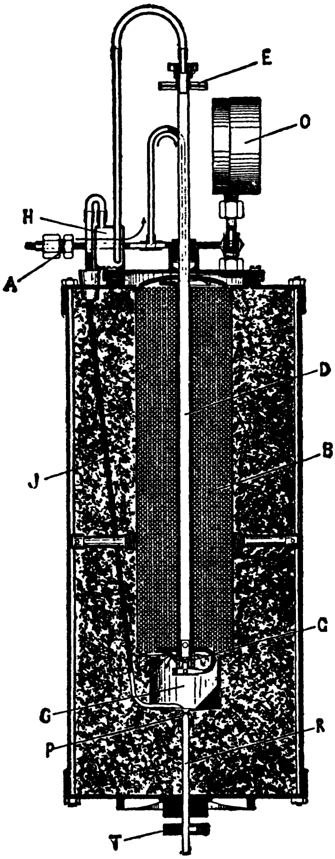


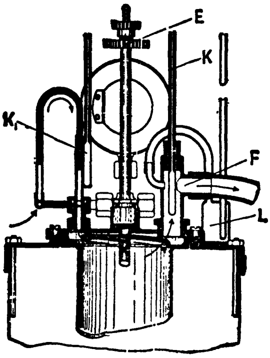
FIG. 57.—British Oxygen Co.'s air liquefying apparatus.

Figs. 57-61 show details of the British Oxygen Company's small Laboratory Liquid Air Plant.

The apparatus is capable of working continuously with a compressor able to deliver air at a pressure of 100-120 atms. It begins to liquefy air in 6-10 minutes after its admission, and produces about 1 litre of liquid air per hour.



Full-length sectional view of air liquefier.



Section of air liquefier.

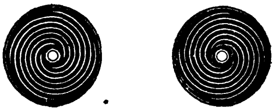


Diagram showing arrangement of regenerator coils.

FIG. 58.

The general arrangement of the plant is shown in Fig. 61, and the method of operation is as follows :—

Before commencing to work, make tight connections from the compressor high-pressure outlet to the inlet of the high-pressure purifier and from the outlet of the latter to the inlet of the liquefier. It is strongly recommended that the outlet of the liquefier F should be connected by a rubber tube with the inlet of the low-pressure purifier. This arrangement makes the charge of the high-pressure purifier last a long time without renewal, and the low-pressure purifier is made large enough to last equally long without recharging.

Air is drawn into the compressor through the large purifier, Fig. 60, which contains slaked lime by which carbon dioxide is absorbed. From the compressor the air is forced at a pressure of about 2000 lbs. per sq. in., first through a separating vessel in which most of the water used as a lubricant is separated out, and afterwards through the pressure purifier, Fig. 59, containing caustic potash in which all remaining traces of moisture and carbon dioxide are absorbed.

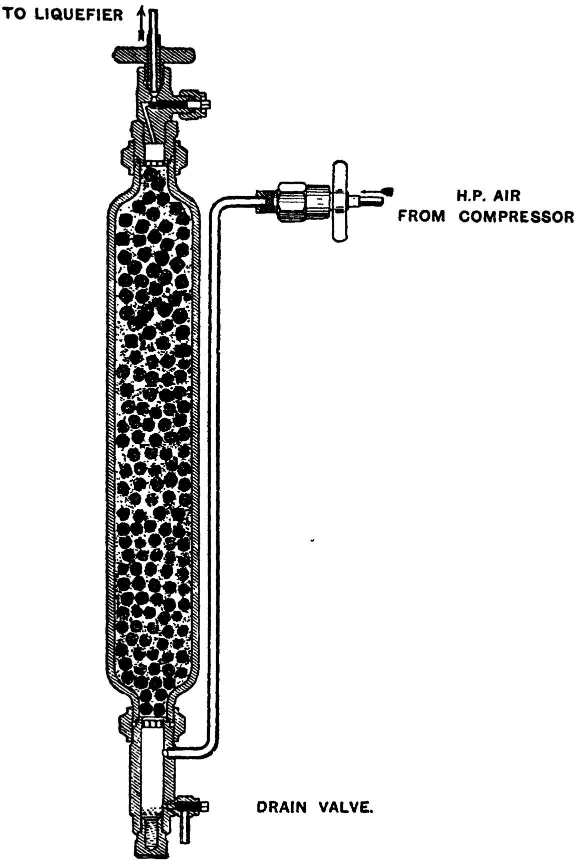


FIG. 59.—H.P. purifier bottle for liquid air plant.

The compressed air, thus freed of moisture and carbon dioxide, passes into the regenerator coils B, through the connection A. It travels down the coils and is allowed to escape through the valve C, which is regulated by a hollow spindle D, to which a hand wheel E is attached on the top of the apparatus.

Let the compressor begin to work with all the valves of connecting pipes and liquefier freely open, including the expansion valve C and the discharge valve P. The air should then be allowed to blow through for a few minutes in order to remove all traces of moisture from the coils. Then close the discharge valve P and close or nearly close the expansion valve C until the compressor raises the pressure to about 150 atms. Then open the expansion valve C gently till a moderate stream of from 5 to 8 cu. ft. per min. passes from the outlet F of the liquefier. The pressure at the outlet is indicated by the glycerine gauge L, and this pressure should be between 6-9 ins. of glycerine. Glycerine is more suitable than water for this gauge, because its viscosity makes it less liable to jumping, and its weight makes a shorter column suffice. A little observation will show the rate, as indicated by the glycerine gauge, at which the air should be allowed to expand for the most profitable production of liquid.

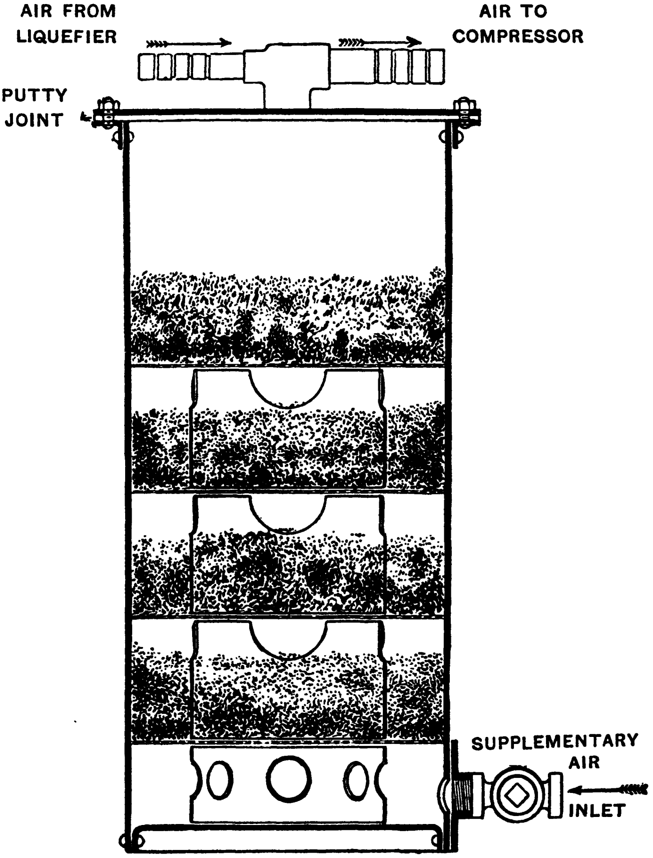


FIG. 60.—L.P. lime purifier for liquid air plant.

The air released through the valve C immediately expands down to atmospheric pressure or thereabouts, and travels back over the regenerator coils B, finally escaping either into the atmosphere direct through the passage F, or back into the compressor, to be recompressed.

The expanded air acts with a self-intensive cooling effect on the compressed air, which is passing down through the coil in the manner already described, and the efficiency of the apparatus is such that in 6 to 10 mins. part of the air begins to liquefy and collect in the receiver G.

NOTE.—While the apparatus is first cooling down, the discharge valve P should, at intervals of about half a minute, be opened slightly to make sure that it is free, and should then be gently closed again, otherwise the contraction caused by cooling may fasten the valve so that it cannot be opened till the Liquefier is again warmed up.

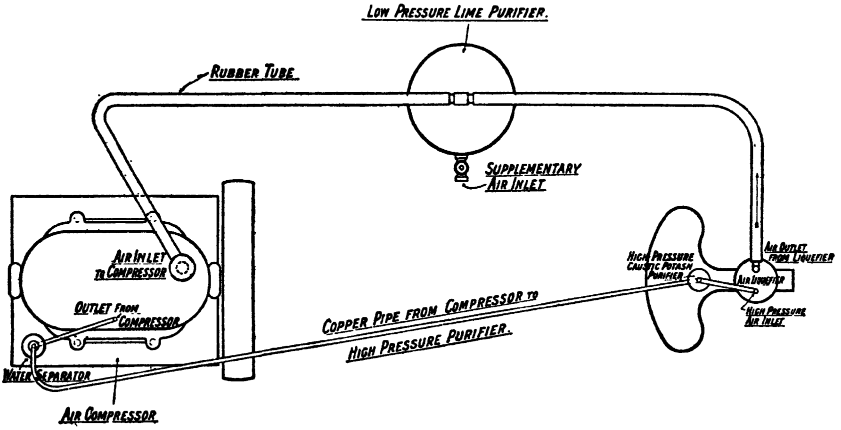


FIG. 61.—General arrangement of liquid air plant. (British Oxygen Co. Ltd.)

When the compressor is working to raise pressure, with expansion valve C closed and when, therefore, no expanded air is escaping, the thermometer plug on the top of the outlet from the air liquefier should be removed to prevent the suction of the compressor drawing air through the glycerine.

Care should be taken to keep all intermediate valves open and to avoid opening the expansion valve C too freely, as by keeping the compressed air at the highest possible pressure as far as valve C, the greatest possible fall of pressure on expansion is obtained.

NOTE.—In completely closing the expansion valve care should be taken to do it gently, as the screw is powerful and violence might injure the tubes which support the valve seat. It should also be opened gently to avoid a sudden rise of pressure in the expansion chamber. Violence should also be avoided in opening and closing the discharge valve P.

The total capacity of the liquid receiver G is $7\frac{3}{4}$ cu. ins., or 127 c.c., and to avoid overflowing under the influence of the blast from the expansion valve the receiver should be emptied when it contains 100 c.c., i.e. when the liquid is 1⅜ ins. or 3½ cm. deep. This is indicated by the column of coloured water in the small gauge H. This gauge communicates with the receiver by means of the pipe J and the hollow spindle D of the expansion valve C. When liquid air collects in the receiver G it compresses the air in the pipe J, and so displaces the coloured water in the glass gauge H, causing it to rise in the vertical glass indicating tube which is attached to it.

When it is desired to withdraw liquid air from the receiver G, the valve P at the bottom of the receiver is opened by turning the hand wheel T, the liquid then enters the hollow spindle R down which it flows into a portable vacuum vessel, in which it is collected.

K is a thermometer which can be used to register the temperature of the air leaving the liquefier.

K_1 is a socket in which a thermometer can be placed to register the temperature of the compressed air as it enters the regenerator coils.

O is a pressure gauge to register the pressure of the compressed air as it enters the regenerator coils.

After concluding an operation, before the pressure has quite run down, partially open the valve at the bottom of the high-pressure purifier, to allow water with dissolved caustic potash to escape.

British Oxygen Co.'s Hydrogen Liquefying Apparatus for Laboratories.

It has been found that hydrogen, when compressed at normal temperatures and allowed to expand in an apparatus like the air liquefier, does not become cooled, but, on the contrary, slightly heated. When, however, its temperature is reduced to − 80° C., or lower, before it enters the regenerator coil, it becomes further cooled on free expansion, so that the principle of self-intensive cooling employed in the air liquefier can then be applied to the liquefaction of this gas.

In order to liquefy hydrogen it is therefore necessary to employ a supplementary cooling apparatus, and the illustrations 62, 63, 64 show in elevation and section a hydrogen liquefier manufactured by the British Oxygen Company to the designs of Professor Morris W. Travers.

It is desirable to note that as the pre-cooling of the hydrogen just mentioned is obtained by the evaporation of liquid air, and as a considerable quantity of liquid air is required, a complete installation for liquefying hydrogen includes an air liquefier. Liquid air *can* be first produced in the hydrogen liquefier if desired, but this practice is not recommended. The hydrogen liquefier is not suitable or efficient for this purpose, and as it is necessary on the grounds of safety and efficiency to remove every trace of air from the purifying vessel, coils, pipes and passages before commencing the liquefaction of hydrogen, the use of the same apparatus for both purposes involves exceptional care and precautions in working.

On the other hand, the same compressor may be employed with both the air and hydrogen liquefiers. The ordinary air compressor has, however, to be slightly modified in construction to make its use with either gas such that it is not possible to get any trace of air mixed with the hydrogen. If a trace of air should be present in the hydrogen the regenerator coils are liable to become blocked by the air solidifying under the low temperature involved in the liquefaction of hydrogen.

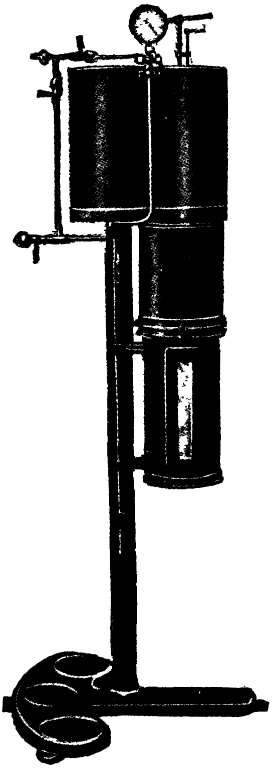


FIG. 62.—British Oxygen Co.'s hydrogen liquefying apparatus.

The sectional elevation shows the general construction of the hydrogen liquefier. Hydrogen is drawn from a suitable gasholder and compressed to a pressure of about 150 atms. It is then passed through a purifier containing caustic potash in order to remove any moisture it may have absorbed in the compressor. It then enters the lower end of the coils in the chamber A, where it is cooled by the cold hydrogen returning to the gasholder. It then passes into the top of the coils in the chamber B. This chamber is filled with liquid air, so that by the time the compressed hydrogen has reached the lower end of the coils in chamber B it is cooled down to the temperature of liquid air, viz. — 190° C. The cold compressed gas then passes into the coils contained in the chamber C into which liquid air is allowed to drop through a small valve regulated by a spindle extending to the top of the apparatus. A partial vacuum is maintained in the chamber C by means of a small exhaust pump connected to the pipe D so that the liquid air passing into the chamber is evaporated *in vacuo*, thus reducing the temperature below — 200° C. The compressed hydrogen, still further reduced in temperature, then enters the regenerator coil E. This coil is contained in a silvered glass vacuum vessel with an opening at the lower end of it. The bottom of the regenerator coil is attached to a valve regulated by a spindle extending to the top of the apparatus, and through this valve the compressed hydrogen finally escapes and expands to normal atmospheric pressure, or, more strictly speaking, to the slight pressure of the gasholder to which the bulk of the hydrogen returns. On its way back to the holder, however, it is caused to pass over the regenerator coil E with self-intensive cooling effect. It then passes round the outside of the chambers C and B into the chamber A, where it acts with further cooling effect on the incoming hydrogen in the manner already explained. Thus the hydrogen returning to the holder is only a few degrees colder than when it entered the coils. The remaining hydrogen has been liquefied at the point of expansion and collects in the vacuum vessel K.

The efficiency of the liquefier is such that liquid hydrogen begins to collect in the vessel K a few minutes after the apparatus is started. As liquid hydrogen cannot be drawn off through a stop-cock without great loss, special arrangements have to be made for collecting it. The use of a stop-cock is obviated by collecting the liquid in the receiver K immediately it is formed in the bottom of the vacuum vessel surrounding the regenerator coil E. The receiver K is contained in a separate metal box below the apparatus. This box has glass windows at the front and back, so that the process of liquefaction can be watched. It is held in place by hinged clamping bolts which compress a rubber ring between two flanges so as to form a gas-tight joint, and it is so arranged that when these bolts are released it can be lowered on a slide L and turned independently, so that the receiver K can be readily changed and the box returned

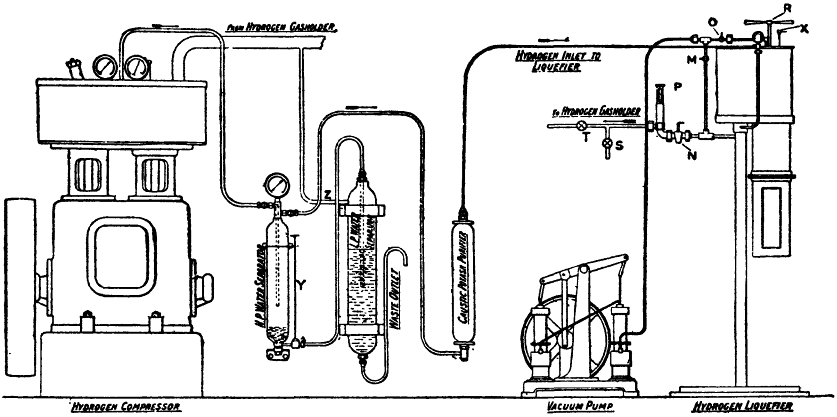


FIG. 63.—General arrangement of hydrogen liquefaction apparatus. (British Oxygen Co. Ltd.).

to its original position without stopping or in any way disarranging the apparatus.

The liquefier is capable of producing about 2 litres of liquid hydrogen per hour, and about 5 litres of liquid air are required in the production of 1 litre of hydrogen.

As all unliquefied hydrogen is returned to the gasholder very little is lost, and about 100 ft. of hydrogen is sufficient for an experiment. A gasholder of this capacity is therefore required, together with a small hydrogen generating plant by which the requisite quantity of gas can be prepared from pure zinc and pure dilute sulphuric acid. As the purity of the gas is a matter of great importance, ordinary commercial hydrogen obtainable in cylinders is not recommended for this purpose.

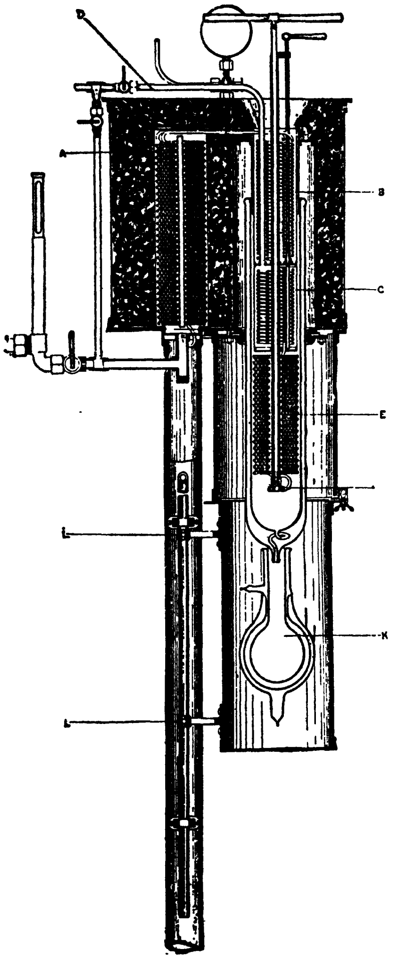


Fig. 64.—Section of hydrogen liquefier.

Directions for Working the British Oxygen Co.'s Hydrogen Liquefier.

Working.

Before starting the hydrogen liquefier it is necessary to have about 5 litres of liquid air ready in reserve for every litre of liquid hydrogen that is required, although more liquid air is necessary for the first litre of hydrogen produced than for subsequent quantities.

In order to cool down the apparatus to the temperature of liquid air, a vessel containing liquid air must be placed at the bottom of the apparatus in place of the hydrogen collecting vessel K, as indicated in sectional view of apparatus.

A pipe extending well into the liquid air should be attached to the outlet at the bottom of the long silvered cylindrical vessel. Then make sure that the valve N is closed, and open valves M and O, thus connecting the whole of the interchanger to the Geryk vacuum pump. Pour some liquid air into the chamber B, and slightly open the regulating valve X to allow some liquid air to trickle into the chamber C. Then start the vacuum pump so as to draw the liquid air or air vapours into the lower part of the apparatus. When sufficient liquid air or vapour has been drawn into the apparatus to cool the whole of it down to the lowest temperature thus attainable, the vessel K must be removed, emptied and replaced. Liquid air must still, however, be retained in the chamber B and the valve X regulated to allow some liquid air to trickle into the chamber C.

The hydrogen compressor may now be started and the regulating valve R slightly opened so as to allow a small quantity of hydrogen to pass and expel all air from the separator through the valve N leading to the vacuum chamber, care being taken to open valve S and close T.

Caution.

This operation is of great importance in order to guard against the possibility of any air passing to the gasholder or compressor.

When sufficient hydrogen has passed through the apparatus to ensure that it has been cleared of air, close valve M and open valve N in order that hydrogen leaving the apparatus returns to the gasholder. The regulator R must now be adjusted so as to maintain a regular supply of compressed hydrogen at a pressure of 150 atms. The flow of gaseous hydrogen leaving the liquefier at N can be judged by the position of the indicator P.

The chamber B must all this time be kept charged with liquid air. After a few minutes' work it will be found that liquid hydrogen collects in the vessel K.

PLANT FOR THE PRODUCTION OF OXYGEN AND NITROGEN ON THE CLAUDE PRINCIPLE.

The following is a description of the well-known Claude air separation process, and I am indebted to " L'Air Liquide " for the information.

The separation of oxygen and nitrogen from atmospheric air is effected by partial liquefaction of its constituents followed by rectification.

Such an apparatus, therefore, comprises three essential features :—

(1) Heat exchangers whereby the gas entering the apparatus is cooled by the various fractions leaving the apparatus.

(2) A source of low temperature, which is provided in the Claude process by an expansion engine, whereby the compressed gas is expanded and cooled by driving the expansion engine and doing useful external work.

(3) An arrangement for rectifying the condensed cold liquids.

The principle of the Claude process is given in Fig. 65, and is as follows :—

1. *Heat Exchanger.*

Air compressed to about 15 atms., from which carbon dioxide and water have been removed, enters the apparatus at the base of the heat exchanger.

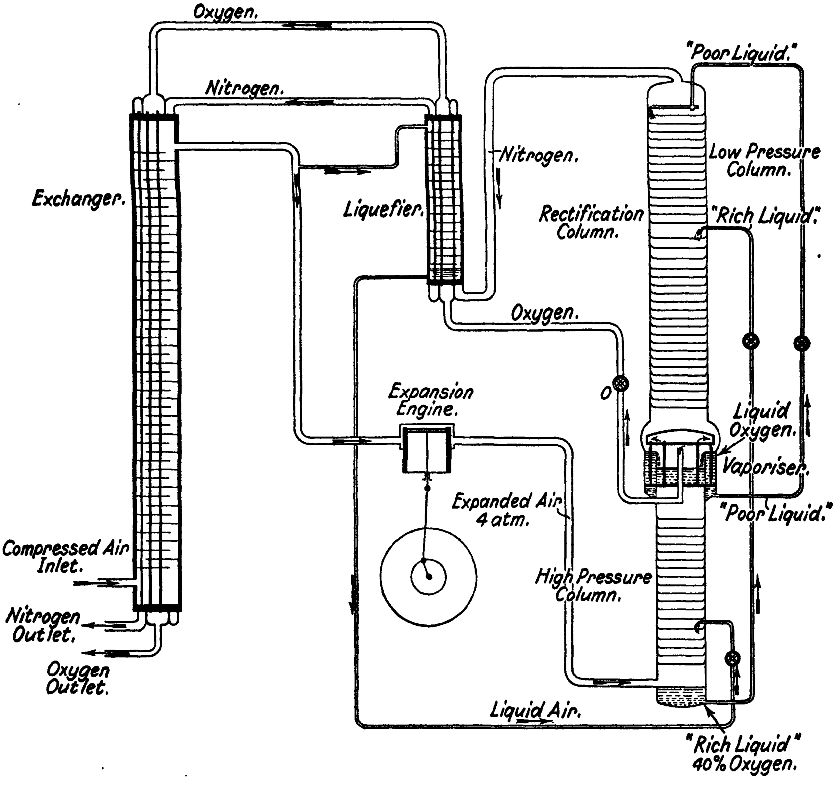


FIG. 65.—Claude air separation plant.

This exchanger comprises a tubular nest, with small bore copper tubes, fitted inside the interior of a steel casing, capable of withstanding the air pressure. The air passes from the bottom to the top in the space between the casing and the tubes. Baffle plates are provided to assist heat transmission, and to ensure good contact between the air and the tubes.

In counter flow to the incoming air, oxygen and nitrogen (separated in the plant and cooled to a very low temperature and at pressures but little above that of the atmosphere) pass down these tubes on their way out of the apparatus. The oxygen and nitrogen streams cool the incoming compressed air, and are themselves heated to practically the air temperature.

2. *Liquefaction.*

The compressed air leaves the heat exchanger at a temperature of — 120° C. The greater portion of this compressed air passes to the expansion engine, and the rest is liquefied in the liquefier. The liquefier consists of a tubular nest of almost the same design as that of the exchanger, but the dimensions are much smaller. The liquefier is cooled by the separated very cold oxygen and nitrogen which flow in counter current to the compressed air on their way to the heat exchanger. This is clear from the drawing. In this way the cold nitrogen and oxygen are warmed up a little before reaching the heat exchanger, so that the air leaving the latter is at a sufficiently high temperature to render the effect of the cooling of the majority of the air by the expansion engine as great as possible.

The liquid air from the bottom of the liquefier is led to the centre of the high-pressure (4 atms.) rectification column.

3. *The Expansion Engine.*

This is an air engine and the compressed air (15 atms.) is expanded within it, with the production of external work to a pressure of 4 atms., and in so doing is cooled considerably.

4. *High-Pressure Rectification Column.*

The cold air from the expansion engine is led to the base of the high-pressure rectification column. Rectification takes place between the liquid air from the liquefier and the cold air from the expansion engine, with the result that the liquid reaching the bottom of the column comprises 40 per cent. oxygen and is known as "rich liquid."

The portion of the expanded air not liquefied in this column is liquefied at the vaporiser by cooling in the tubes through the oxygen bath, and condenses to form a "poor liquid," a liquid poor in oxygen, since rectification in the high-pressure column removed a large proportion of the oxygen from it.

5. *Vaporiser.*

Having now obtained two portions of "liquid air" one rich in oxygen and one rich in nitrogen, further rectification takes place in the "Low-pressure Column."

The vaporiser consists of a nest of tubes surrounded by liquid oxygen which is supplied by the low-pressure column.

It is to be noted that the nitrogen enriched air circulating in the tubes of the vaporiser at a pressure of 4 atms. is warmer than the oxygen in the bath surrounding the tubes. Hence, an exchange of heat takes place which, in the first instance, causes the oxygen to evaporate and leave the system by the valve O, and secondly the nitrogen enriched air is liquefied to form the " poor liquid."

6. *Low-pressure Rectification Column.*

The " rich liquid " is admitted to the centre of the low-pressure rectification column, as seen in the figure. The liquid falls down through the column, and in so doing loses nitrogen by evaporation, until finally pure liquid oxygen falls to the oxygen bath.

The gas reaching the top of the low-pressure rectification column is washed by the poor liquid, so that only pure nitrogen finally escapes from the top of the column to pass through the liquefier on its way to the heat exchanger.

Claude plants of this type are built in sizes from 240 cu. metres to 3000 cu. metres (just over 100,000 cu. ft.) of free air per hour. The working pressure required is inversely proportional to the size of the plant, and varies between 12-18 atms.

LINDE AIR SEPARATION PLANTS.

Another important type of air separation plant is that built by the Linde Eismaschinen A.G. of München, and is illustrated diagrammatically in Figs. 66, 67.

Taking first Fig. 66, this is a small plant for the separation of oxygen and nitrogen from air by single rectification and without pre-cooling. Air is drawn in at (1), where it is cleaned and filtered. The pressure is then raised to 200 atms. in four stages, with inter-cooling. When the plant is cooled down and actually producing liquid air, the pressure is reduced to 50-65 atms.

Two oil and water separating bottles are fitted (3) and the carbonic acid content of the air is removed by washing with caustic soda under pressure in (4). Final traces of water vapour are removed by passing the compressed air over anhydrous calcium chloride in (5). Separation of the oxygen and nitrogen from the liquefied air takes place in (6) and the separated constituents pass out of the plant as indicated.

Fig. 67 shows a much larger Linde air separation plant for a maximum working pressure of 60 atms. and in which pre-cooling of the air is employed before liquefaction.

In this case the initial air pressure required is 60 atms., which falls to 20-30 atms. when liquefaction commences. After oil and carbonic acid have been removed as previously described in (3) and (4), a counter current cooler (6) cools the compressed air down to − 20° C., or so. By means of an ammonia refrigeration plant (8) the air is further cooled down to − 40° C., in (7). After double rectification the oxygen and nitrogen pass out through the heat exchangers as shown.

It will be noted that the Linde process does not employ an expansion engine (as is the case with the Claude system), but is operated upon the principle of the Joule-Thomson effect similar to that described in the case of the British Oxygen Company's liquid air plant. This principle is shown clearly for reference purposes in Fig. 68.

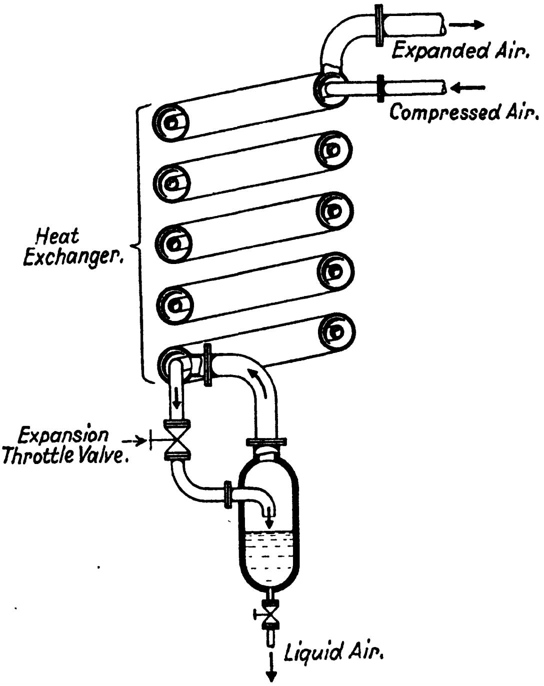


FIG. 68.—Heat interchange in air separation by liquefaction.

The expanded air cools the incoming compressed air, which is further cooled by sudden expansion at the throttle valve. This self intensive cooling finally results in the liquefaction of the air issuing from the throttle valve.

Regarding the actual separation of the main constituents of air (oxygen and nitrogen) as indicated previously, there are two types built by Linde, one employing single rectification and the other double rectification. Fig. 69 shows the single rectification type. Separation as in the Claude column depends upon the difference in boiling-points of the oxygen and nitrogen.

Liquid air is allowed to fall down the column (*b*). The liquid on its downward path washes most of the oxygen out of the vapours rising in the opposite direction, so that the vapours gradually become richer in nitrogen as they rise, and at the same time the liquid on its way down increases in oxygen content until finally almost pure oxygen settles at the bottom of the rectification column. Part of the vapours from this liquid oxygen bath are sent up the column to assist rectification, and the remainder issues from the plant in a continuous gaseous stream as the oxygen product of the plant.

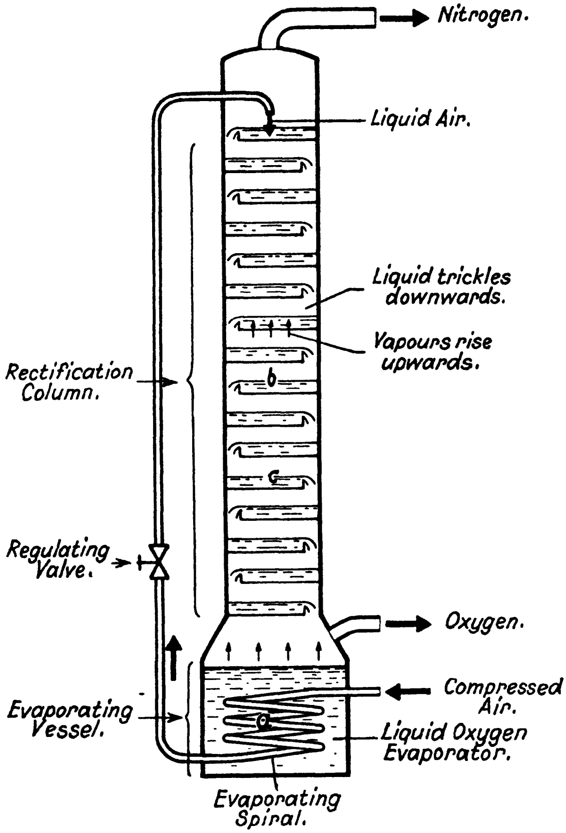


FIG. 69.—Linde single rectification column.

The vapours drawn away from the top of a column of this type cannot be completely freed from oxygen, and in practice about 7 per cent. by volume of oxygen is present in the nitrogen. To avoid this loss, double rectification is employed, and this is illustrated in Fig. 70. It is similar in many respects to that previously described in the case of the Claude process.

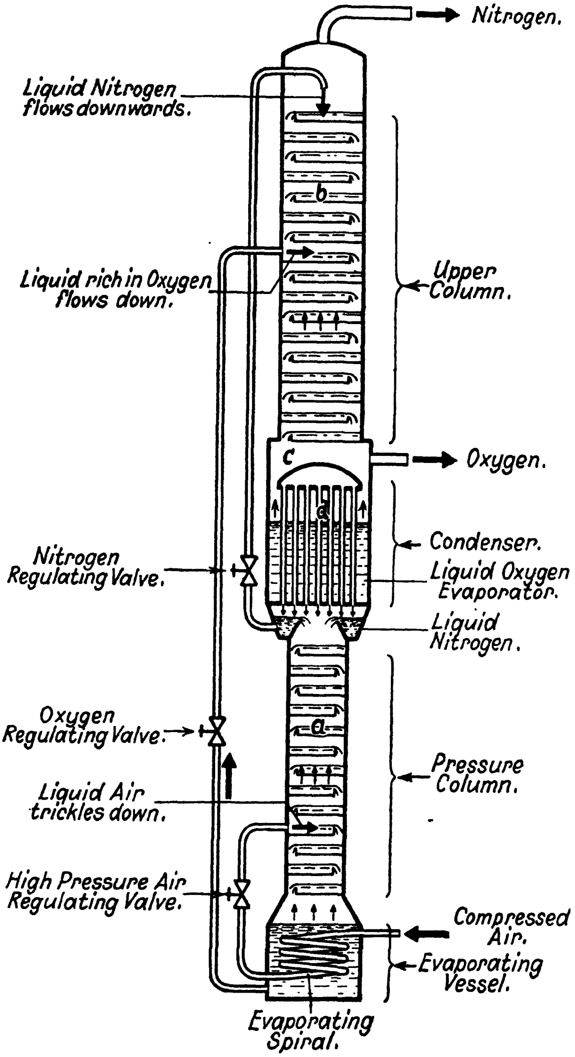

Nitrogen.
Liquid Nitrogen flows downwards.
b
Liquid rich in Oxygen flows down.
Upper Column.
c
Oxygen.
d
Condenser.
Nitrogen Regulating Valve.
Liquid Oxygen Evaporator.
Liquid Nitrogen.
a
Oxygen Regulating Valve.
Pressure Column.
Liquid Air trickles down.
High Pressure Air Regulating Valve.
Compressed Air.
Evaporating Vessel.
Evaporating Spiral.

FIG. 70.—Linde double rectification column.

Regarding the various types of Linde plant, the smaller designs (where first cost is important) employ high-pressure compression without pre-cooling and with single rectification. The large industrial types employ pre-cooling and double rectification, so that the greatest economy in operation is attained.

A recent interesting development of the liquefaction of air by the use of pressure is that of the application of this process to the oxygen enrichment of the air supplied to metallurgical furnaces. This development is due to M. Frankl in co-operation with the Linde and L'Air Liquide Companies, and was recently described by M. Georges Claude (*Compte Rendus*, 1932, **195**, 919).

The subject of cheap oxygen or oxygen enriched air is of great interest and importance to metallurgical and gas engineers. For example, one benefit resulting from oxygen enriched air supply to blast furnaces would be the higher calorific value of the blast furnace gas by elimination of part of the unwanted nitrogen. Furthermore, the removal of part of the nitrogen from the blast air would eliminate at least part of the expensive hot blast stove equipment, which at present consumes about one-third of the total heat value of the gas produced in the blast furnace.

Another example where oxygen enriched air would be of great benefit is the open hearth furnace, e.g. where very high temperatures are desired coupled with a reducing atmosphere. By enriching the air, the total volume of gas passing through the furnace per unit weight of fuel consumed is reduced considerably, and this would greatly facilitate heat exchange and fuel conservation. Other examples which would benefit by oxygen enriched air are the copper blast furnace running on sulphides.

In the gas-making industry it is obvious that oxygen enriched air will have great advantages, and in this connection Finlayson (*Trans. Inst. Chem. Eng.*, 1923, **1**, 76) carried out numerous experiments dealing with the oxygen enrichment of air, and concluded that the cheapest process to produce an air supply containing 40 per cent. oxygen was by the pressure fractionation process, i.e. a process depending upon the preferential solubility of oxygen in water, and also other solvents such as methyl and ethyl alcohol, oils, etc. The scheme proposed was as follows :—

The plant consists of two vessels, each fitted with efficient stirrers and a gas offtake at the top. Each vessel is full of suitable oil and the agitators are running. Air is pumped into No. 1 vessel until the pressure is 135 lbs. per sq. in. Further gas (blow-back gas) is pumped into No. 1 until the pressure is 150 lbs. per sq. in. We thus have No. 1 saturated at 150 lbs. with a gas containing about 22 per cent. oxygen ready for fractionation. The fractionation is carried out as follows, equilibrium being regarded as existing throughout. The pressure is allowed to fall to 75 lbs. The gas evolved is passed through a high-pressure blower for the recovery of as much power as possible, and is then blown to waste.

The pressure is then allowed to fall to 36 lbs. through the low-pressure blower, also for power recovery. This second portion is also valueless. The pressure is then allowed to fall to 20 lbs. This gas contains about 25 per cent. oxygen, and is compressed and pumped into No. 2 vessel during the solution stage, this being the blow-back gas. The pressure is allowed then to fall to 1 lb. absolute, the gas evolved being of the mean composition of 40 per cent. oxygen.

The main cost of the process lies in the compression of air, so that efficient means would have to be provided for the recovery of the power from the compressed air. A study of the economics of the process has shown that it is cheapest to dissolve all the air compressed, and start the fractionation with 21 per cent. of oxygen in solution. This start is the factor which determines the higher limit for the final oxygen strength. Thus, if it were possible to start with 30 per cent. oxygen in solution, a final oxygen of 60-70 per cent. strength would be obtained.

A further scheme for improving the pressure fractionation effect in order to give strong oxygen gas at an economic figure has been considered. This depends upon the use of methyl or ethyl alcohols at low temperatures as solvent. According to some work, it appears that the solubility of oxygen increases with fall in temperature, whilst the solubility of nitrogen decreases. In this way, the differential solubility becomes greater, leading to a sharper fractionation.

To return to the recent paper on this subject by M. Georges Claude, this problem of oxygen enriched air was undertaken by M. Frankl, using the liquefaction of air as the basis of the supply of the oxygen.

Until the recent invention of M. Frankl, all air liquefaction plants utilised heat exchangers to economise power, and in spite of the most careful design, the difference between the gases entering and leaving the exchangers was 5-6° C.

M. Frankl suggested replacing these heat exchangers by " regenerators " exactly as conceived by Siemens many years ago in connection with heat conservation in metallurgical furnace work.

In the case of this air separation plant, this principle is utilised by passing alternately and in opposite directions in each regenerator, one of the gases separated from air (oxygen or nitrogen) and then a corresponding amount of the incoming compressed air. For *each* constituent (oxygen or nitrogen) there are *two* regenerators.

Whilst the oxygen, for example, returning from the liquid air fractionating column passes in one direction through one regenerator and thus cooling it, and is thereby itself heated, the corresponding fraction of the incoming compressed air passing to the column is proceeding through the other " oxygen " regenerator in the other direction, and is thereby cooled. At intervals of 100 seconds or so, automatic valves change over the above procedure.

The gas contact surface in the regenerators is made as large as possible by filling them with metal ribbons.

In this way the difference between the gases entering and leaving the plant is reduced to 1·25° C., and in consequence the pressure required to operate the air liquefaction plant falls from 12 atms. to 5 atms. with a corresponding reduction in power costs.

A plant built by Linde-L'Air Liquide on these lines suggested by M. Frankl is operating at Oberhausen and treats 11,000 cu. metres (390,000 cu. ft.) of air per hour. The plant is used to enrich with oxygen the air supply to a small blast furnace and the cost of supplying air with a 45 per cent. oxygen content is about 0·120 kilowatt hour per cu. metre of such air. The results are stated to be most satisfactory.

It will be obvious that it is not possible to produce pure oxygen or nitrogen by the method suggested by M. Frankl, because of the means adopted for recuperation. The recuperators being alternately filled with oxygen or air—nitrogen or air leads to contamination of the first runnings. For oxygen enrichment purposes or where the purity of the gases is not of great importance, this process appears to have a very definite future.

MANUFACTURE OF HYDROGEN.

Of recent years, the attention of many industrial organisations has been directed to the production of large quantities of pure gases for the many synthetic operations now used in chemical manufacture. Of these, perhaps the chief interest is that of hydrogen which plays such a great part in so many catalytic processes.

The methods of producing hydrogen for its many industrial uses may be conveniently classified as follows :—

(1) Electrolysis of water, either at atmospheric or increased pressure.
(2) From water gas by the steam iron process.
(3) From water gas by the catalytic process.
(4) From coke oven gas or water gas by the Linde or Claude process.
(5) From methane.

Pressure plays a very important rôle in many of the above processes, and also in connection with the other gases used in synthetic processes. (For example, the nitrogen used for the manufacture of synthetic ammonia is often obtained by the liquefaction of air.)

Each of the above methods of producing hydrogen will now be discussed in detail. For much of the information contained in the next few pages I am indebted to the Institute of Chemical

Engineers for permission to abstract it from a paper by Dr. E. F. Armstrong, which appeared in the *Transactions* of the Institution in 1931.

A COMPARISON OF THE MERITS OF THE VARIOUS SOURCES OF HYDROGEN ON A LARGE SCALE.

The situation regarding the various methods of producing hydrogen is clearly indicated by a table which is taken from Colonel Pollitt's paper before the World Power Conference in Berlin (1930).

PERCENTAGES OF SYNTHETIC AMMONIA PRODUCED FROM HYDROGEN DERIVED FROM VARIOUS PROCESSES.

Percentage of World Total Synthetic Ammonia made with Hydrogen derived from	Fertiliser Year.				
	1926-7.	1927-8.	1928-9.	1929-30.	1930-31.
Water gas	89·0	84·1	77·3	69·7	67·9
Coke oven gas . . .	3·0	5·8	11·1	14·2	15·8
Electrolysis of water . .	6·4	8·8	10·5	15·2	15·4
Other processes (electrolysis of brine, fermentation, etc.)	1·6	1·3	1·1	·9	·9
	100	100	100	100	100

It shows that the percentage of hydrogen made by the water gas method is falling, that from coke oven gas is rising, whilst that by electrolysis is rising very slightly. Colonel Pollitt does not regard electrolytic hydrogen as a permanently serious competitor to hydrogen from coal.

Colonel Pollitt has set out clearly the advantages of water gas, including the fact that hydrogen so obtained is the main product of a reaction, and not the by-product of a separate industry, and possesses the further advantage of freedom of site.

He gives the capital costs of the three processes :—

Source of Hydrogen.	£ per m. Ton Year of NH_3.		
	Plant.	Buildings.	Total.
Electrolytic	40·8	5·2	46·0
Water gas	30·5	4·6	35·1
Coke oven gas	29·0	4·0	33·0
,, ,, ,, revised	—	—	15·2

and the working costs of the manufacture of 1 ton of ammonia (NH_3) in the form of 25 per cent. liquor :—

Source of Hydrogen.	Cost of NH_3 per m. Ton.
H.T. A.C. current at 0·05d. per K.W.H.	7·0
,, ,, ,, 0·10 ,, ,,	9·0
,, ,, ,, 0·15 ,, ,,	11·7
Coke oven gas	9·0
Water gas	7·2
Revised figure for coke oven gas . .	6·0

Hydrogen from Methane (Natural Gas).

In the United States and elsewhere to-day almost unlimited quantities of methane are available in the form of natural gas. Consequently attention has been paid to the conversion of this into hydrogen by means of the reaction

$$2H_2O + CH_4 = CO_2 + 4H_2.$$

This may be effected by nickel-magnesia or nickel-alumina catalysts. The following patents are quoted as examples of the type of process suggested.

Hydrogen is obtained by subjecting a 2 : 1 steam methane mixture at 150 atms. and a temperature less than 600° C. to the action of a nickel-magnesia catalyst, the magnesia being present in the proportion of at least 1 mol. of magnesia to 1 mol. of methane in the gas mixture.

Methane is passed over a nickel-alumina catalyst at a temperature in excess of 1200° F. with steam till the activity of the catalyst diminishes and then steam alone is passed till the activity of the catalyst is restored, when the methane is again passed over it.

Hydrogen is obtained by the alternate supply of air and hydrocarbon gas, with or without steam, to a bed of coke or refractory material, the blow gases being burnt in an annular chamber surrounding the bed of coke or refractory material, so as to return to the bed a substantial quantity of the heat produced by their combustion.

Hydrocarbons are made to interact with steam at 300-600° C., in presence of such catalysts as nickel, cobalt or iron activated with chromium, vanadium, potassium, magnesium, aluminium or alkaline earth metals, the resulting carbon dioxide being removed.

Imperial Chemical Industries in their projected hydrogenation of coal will make use of the hydrocarbon gases formed in some quantity as a by-product by converting them into hydrogen by treatment with steam, any deficit being made up by ordinary water gas. Sensicle has suggested that if coke oven gas be used as the source of hydrogen for coal hydrogenation, the methane formed together with the excess hydrogen can be returned to the coke oven gas whereby the full burning value, say 2d. a therm, can be obtained for the methane. The problem of surplus coke oven gas is such as to make it well worth while to link up its disposal with the hydrogenation of coal or oils from coal.

These processes are as yet in their infancy, and nothing can be stated in regard to costs. If the hydrogenation of crude oil becomes practised on any scale, they will undoubtedly be developed.

Electrolytic Hydrogen.

Whenever pure hydrogen is required, or hydrogen in small quantities, or even in large quantities in localities where electric power is cheap, its production by electrolysis of 18-20 per cent. caustic soda or of 25-30 per cent. caustic potash solutions is the method frequently chosen. The potash electrolyte is more costly and the diaphragms and insulators not so durable, so that it is usually preferable to use caustic soda. The electrolytic cell is used to produce both gases or either hydrogen or oxygen, but when the total production of both gases can be used the maximum economy is effected.

When making hydrogen, the sale of the other product of electrolysis, oxygen, cannot usually be counted on in the quantities in which it is produced, and so the whole of the cost of the operation has to be borne by the hydrogen. For small quantities under 3000 cu. ft. per hour, electrolytic hydrogen is undoubtedly cheaper than that produced by any other method.

Modern electrolytic plant may be broadly divided into two types —filter press and collecting bell cells. The chief advantage claimed for the former are low first cost and the small floor space required, but they present many difficulties in design. The bell type is represented by the well-known Knowles cell of the International Electrolytic Plant Co., the general and special features of which are well known. The first plant, operated at Bromborough in 1912, remained for many years the world's largest unit battery. Since then, this firm has successfully built many large units. The table on next page taken from the Knowles Cell Co.'s pamphlet gives the electrolytic hydrogen cell constants.

From this the theoretical production per 1000 ampere hours is 16·25 cu. ft. of hydrogen measured wet at 20° C., and 760 mm. The guaranteed figures for a Knowles cell under these conditions are: output 161·4 cu. ft. of hydrogen with an efficiency of 140 K.W.H. per 1000 cu. ft.

Hydrogen Liberated per 1000 amp. hrs.		Amp. hrs. required to Liberate Unit Mass or Volume of Hydrogen.	
Grams	37·65	Per gram	26·56
Pounds	0·0830	Per pound	12,050
Cu. ft. at 20° C. and 760 mm. wet	16·25	Per cu. ft. at 20° C. and 760 mm. wet	61·55
Cu. ft. at 0° C. and 760 mm. dry	14·79	Per cu. ft. at 0° C. and 760 mm. dry	67·61
Cu. m. at 20° C. and 760 mm. wet	0·4604	Per cu. m. at 20° C. and 760 mm. wet	2,171
Cu. m. at 0° C. and 760 mm. dry	0·4189	Per cu. m. at 0° C. and 760 mm. dry	2,387

The guaranteed purity is 99·0 per cent. oxygen and 99·5 per cent. hydrogen. In practice, with ordinary care, 99·6-99·8 per cent. oxygen and 99·8-100 per cent. hydrogen can be regularly obtained.

The practical limits of cell voltage are about 2-2·5 volts, equal to a consumption of 135 K.W.H. to 170 K.W.H. per 1000 cu. ft. of hydrogen produced.

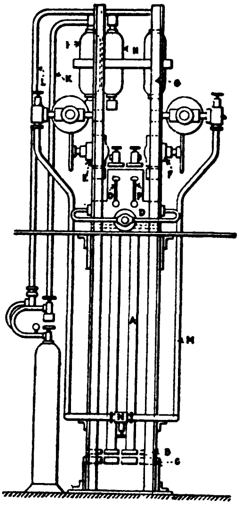


Fig. 71.—Noeggerath high-pressure electrolysis apparatus.

There is another method of producing hydrogen which is becoming commercially significant in connection with chemical processes requiring hydrogen at high pressure, and this is the Noeggerath system of the electrolysis of water under pressure, whereby oxygen and hydrogen can be produced electrolytically at pressures of 200 atms. or so.

A complete account of the process will be found in *Chemical and Metallurgical Engineering*, 1928, **35**, 421, in which the inventor describes a large experimental unit tested during 1927 by the Berlin Technische Hochschule and the German State Railroad. A diagram of this apparatus is seen in Fig. 71. The actual pressure cells are the tubes indicated by A, through the axis of which run the negative nickel electrodes generating the hydrogen. The latter are surrounded each by a concentric separating wall, and the walls in turn by concentric positive electrodes which generate the oxygen. The electrolyte is potassium hydroxide.

The current is supplied to the positive electrodes at B, the vessel itself serving as a conductor. It passes through the separating wall (not shown) to the negative electrode and leaves the cell again at its cover C. For operation at normal voltages the cells are arranged in series in a certain definite order. The oxygen rises up the outer section of the pipe A, collects in the passages of the distributer D, and enters the holder G by valve F, and finally flows to the cylinders through the pipe L.

Completely separated from the oxygen by the intervening wall, the hydrogen rises along the axis of A, collects in the other passages of the distributer D, and flows through the valve E to the holders H and I, and through the pipe K to the cylinders.

The two electrolyte chambers are connected by a compensating line M, to which the make-up water for the electrolyte is fed at N. This compensating line has a large capacity, so that the electrolyte from one half will not run into the other, where there is a difference in pressure. Its great length allows of such small cross-section that the velocity of feed water for the electrolyte greatly surpasses that of the gases tending to enter the compensating line. This is the first application of an elastic compensation on pressure cells. The check valves O and P serve to cut off the cells from possible disturbance should any unforeseen difficulties arise outside.

In tests by the German State Railroad it was found that this apparatus generated 1 cu. metre of gas for an expenditure of energy of 3-3·5 kw., and purity of both gases of 99 per cent. and over was obtainable. It was also found that the cost of generating the gases at high pressure was no more than generating at ordinary pressure. It was also noted that the liberated gas bubbles, which affect the electric path, are compressed as the pressure increases, and due to their reduced volume, lower the resistance and voltage of the electrolyte.

Newitt and Sen have recently carried out a series of experiments with a small type of high-pressure electrolysis apparatus, their object being to develop a small unit to produce hydrogen and oxygen under pressure for use in remote localities where other methods would be quite impossible (*Trans. Inst. Chem. Eng.*, 1932, **10**, 22).

E. P. A. Heinze (*Engineering*, 1933, **135**, 399-400) discusses the possibility of utilising the compressed hydrogen produced by the Noeggerath pressure electrolysis process as a means for distributing power, in view of recent development in engines of the Essen type, which use hydrogen as a fuel. Such engines use about 20 cu. ft. of hydrogen per horse-power hour.

Hydrogen from Water Gas and Producer Gas.

Dr. Krauch of the I.G. published in *Stahl und Eisen* in 1927 a critical statement embodying their experience of the various methods of preparing hydrogen. The I.G. at first tried the Linde method; later they used producer gas and water gas mixed in the proportions to give ammonia, passing it over the Bosch catalyst with steam. Carbon dioxide was washed out, and subsequently recovered and used, and carbon monoxide and sulphur were also removed. In the course of their long practical working with this method, it was so far improved that the steam consumption, for example, was reduced to less than half the quantity originally required.

At one time sulphur impurities were removed by means of active carbon, being recovered in the form of sulphur. This process involves the addition of sufficient air to oxidise the hydrogen sulphide present to sulphur. The impure gas is passed through a bed of activated carbon, in which sulphur accumulates. When a sufficient quantity is reached, the carbon bed is sprayed with a solution of ammonium sulphide, which dissolves the crude sulphur, with the formation of ammonium polysulphide. On boiling this solution, the ammonium sulphide is recovered and sulphur deposited. According to a paper by Carleton Ellis, this process was recently in action at Leuna, and from 20,000 to 40,000 lbs. of sulphur were obtained from it daily.

As a result of removing the sulphur, it is reported that the life and activity of the catalyst and the output of the whole hydrogen plant were materially improved.

The I.G. have examined a number of rival schemes of hydrogen production, particularly the electrolytic, which they found dear even at a price of 0·18d. per K.W.H. in Bavaria, or at 0·06d. to 0·072d. per K.W.H. in Norway. Dr. Krauch also speaks adversely from the point of view of cost of the Messerschmidt steam-iron process, and of that from coke oven gas suggested by Mont Cenis, at that time in its infancy.

More recently, the I.G. have worked out a still cheaper process in which water gas is made from crude brown coal. The principle of this is that a 6 ft. layer of finely divided brown coal is put at the bottom of a producer and kept constantly in motion by an air or steam blast. The fine coal behaves very like a liquid, probably because each tiny particle is evolving gas and is surrounded by a sphere of gas, so that fresh fragments introduced mix immediately with the red-hot bulk and come into the very closest contact with the blast. The mixed gases formed leave the producer at about 1000° F., and their sensible heat is used to dry the raw brown coal. The escaping gas is cooled to about 250° F., and undergoes the usual purification.

The output of this plant and thermal efficiency are stated to be high, and the cost of hydrogen production by it is likely to be materially less.

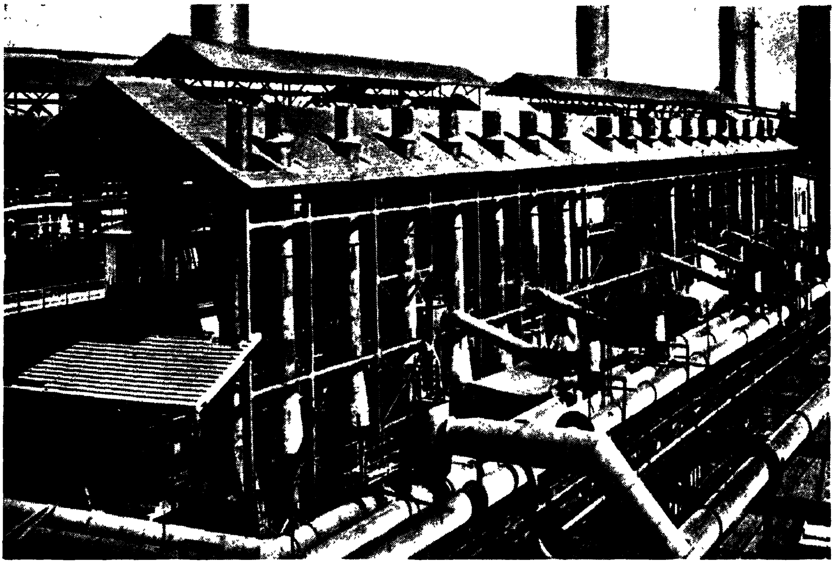


FIG. 72.—I.G. Farbenindustrie, A.G. Leuna gas plant, daily production 88,000,000 cubic feet of gas.

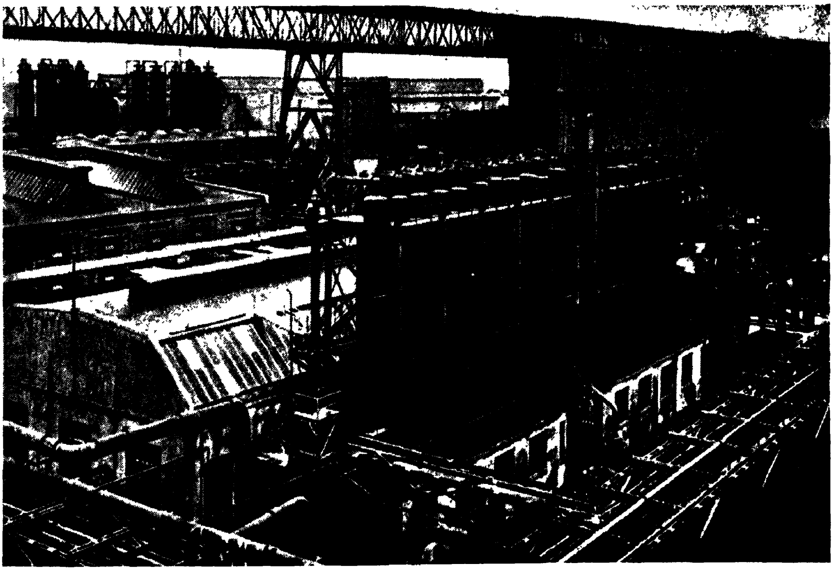


FIG. 73.—I.G. Farbenindustrie, A.G. Leuna works catalytic hydrogen plant.

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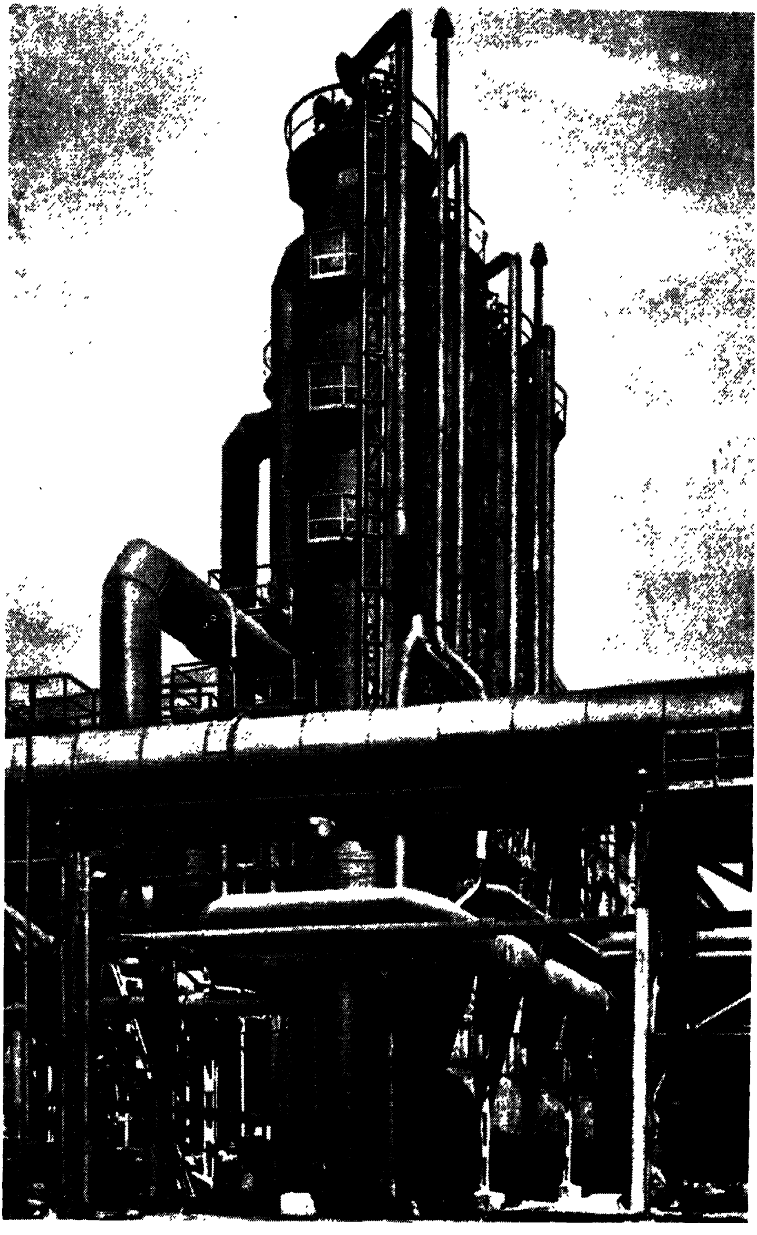

FIG. 74.—Spraying tower for gas purification. (I.G. Farbenindustrie hydrogen plant.)

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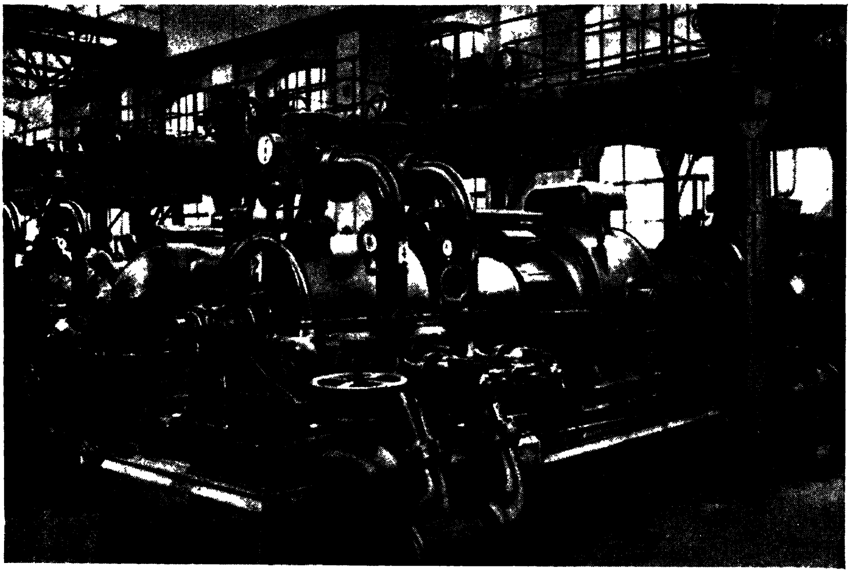
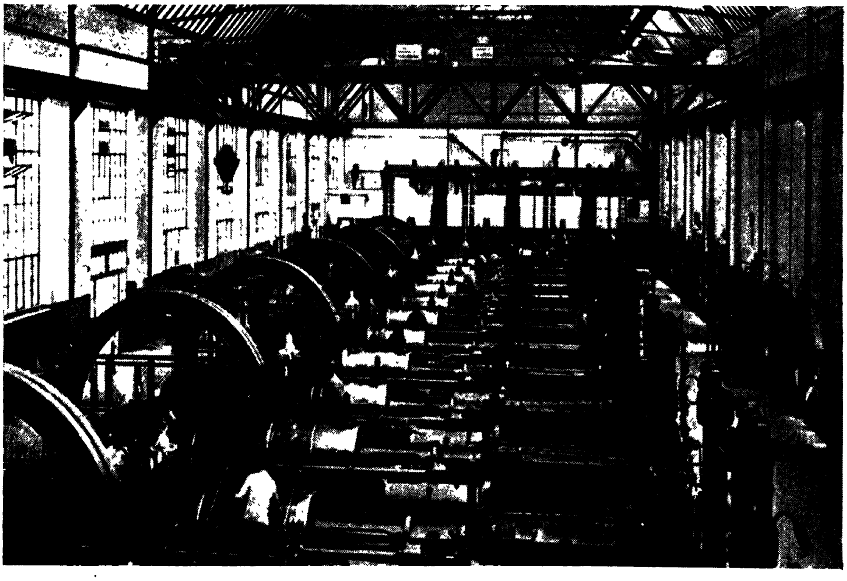


Water compression pumps for gas washing.



High-pressure pumps for gas purification.

Fig. 75.—I.G. Farbenindustrie Hydrogen Plant.

[*To face page* 115.

It is stated that a Winkler producer designed to deal with 1200 tons of raw dried brown coal per 24 hours operates successfully at a load of 750-800 tons per day.

The following information about the method of manufacture of hydrogen by the I.G. Farbenindustrie (which I have received in a communication from the company) will supplement details just given in this respect.

The hydrogen-nitrogen mixture of the Haber-Bosch ammonia process is made at Leuna and Oppau from a mixture of producer gas and water gas. After preliminary purification, the mixture of raw producer-water gas mixture is stored in large gasholders. Sulphur compounds in the raw gases are then completely removed, and the greater proportion of the carbon monoxide present in the gas mixture is converted into carbon dioxide by interaction with steam in the presence of a catalyst, and additional hydrogen is, of course, also produced by this reaction.

The resulting gas mixture consists almost exclusively of three gases, i.e. hydrogen, nitrogen and carbon dioxide. The carbon dioxide is removed by compressing the gas to 25 atms. and washing thoroughly with water under pressure. By reducing the pressure of the water leaving the plant, the carbon dioxide is set free and is used in the manufacture of sulphate.

The gases freed from carbon dioxide are compressed to 200 atms., and at this pressure are washed with a copper salt solution to remove the last traces of carbon monoxide (which, of course, is a deadly poison in so far as the ammonia synthesis catalyst is concerned). The gas then consists of an almost pure mixture of hydrogen and nitrogen. In order to bring the ratio of nitrogen to hydrogen in the mixture up to 1 : 3 pure nitrogen is added ; this additional nitrogen is made from the liquefaction of air by the Linde process.

The illustrations, Figs. 72-75, give a very clear idea of the large operating scale of the Leuna plant of the I.G.

Regarding the various forms of carbon for water gas production the following table is of interest :—

COMPARATIVE CARBON COSTS OF 1000 CU. FT. OF WATER GAS PRODUCED FROM VARIOUS FUELS.

	German Brown Coal.	High Temp. Coke.	L.T. Coke Breeze.	Bituminous Smalls.
Cost per ton at works, shillings .	1·5	18·5	10·0	10·0
Percentage of carbon in fuel . .	30·0	85·0	81·0	75·0
Relative cost per 1000 cu. ft. in pence	1·38	3·96	2·50	3·00

Carbon lost due to liberation of volatile matter during blow period is taken into account.

The object of showing the comparative carbon cost per 1000 cu. ft. of water gas is to draw attention to the important part played by the first cost of the carbon in the form of various kinds of fuel. There is no doubt that, besides the highly developed technique in Germany, the abundance of carbon base in the form of brown coal is a dominating factor in the production of cheap hydrogen. One would imagine that, by making full use of low grade coals or waste carbonaceous materials, the carbon cost in the production of water gas could be very much reduced in this country, and it should not be without the bounds of possibility that sooner or later some method may be devised for rendering these carbon products, which are to-day literally waste, available for water gas and subsequent hydrogen production. The figures do indicate that countries such as Canada and Australia, with their immense brown coal and lignite deposits, should be in an unique position for producing a cheap supply of water gas and hydrogen, eventually rendering these countries less dependent upon an overseas supply of oil. The potentialities of low temperature coke, particularly in view of the fact that it is also more reactive, cannot be overlooked.

Hydrogen from Coke Oven Gas by the Claude Process.

The Claude synthetic ammonia process usually derives its nitrogen from the liquefaction of air by the Claude process, which has already been described. The hydrogen is most frequently obtained from coke oven gas, and Claude has developed a very interesting technique in this connection, based on his experience over many years in the economical liquefaction of air, and the separation of the constituents thereof.

The coke oven gas is first purified to remove the usual by-products, i.e. benzol-tar-ammonia, and the subsequent purification to obtain hydrogen may be divided into three parts, viz. compression, purification, liquefaction (see Fig. 76).

The gas, as delivered from the coke ovens, is, after the preliminary purification, compressed by reciprocating compressors to about 22 atms. in the case of the small units (treating 900 cu. ft. of gas per min.) to 15 atms. for the larger plants which deal with over 5000 cu. ft. per min.

The easily condensable elements of the coke oven gas (benzol, carbon dioxide, hydrogen sulphide, steam, etc.) are then removed as follows :—

The compressed gas is circulated from the bottom to the top of a first column containing a packing which is irrigated with a heavy oil

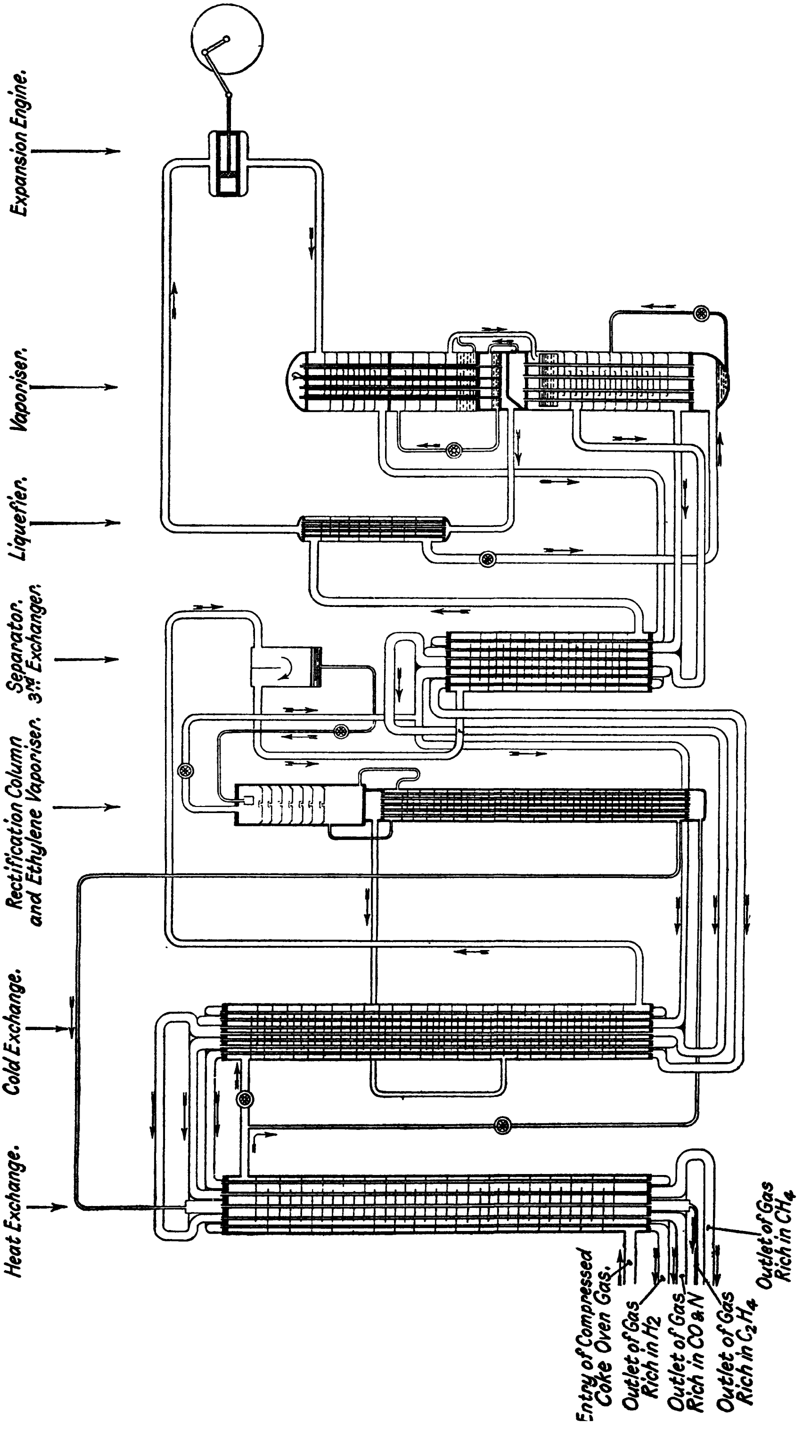

Heat Exchange.
Cold Exchange.
Rectification Column and Ethylene Vaporiser.
Separator. 3rd Exchanger.
Liquefier.
Vaporiser.
Expansion Engine.
Entry of Compressed Coke Oven Gas.
Outlet of Gas Rich in H2
Outlet of Gas Rich in CO & N
Outlet of Gas Rich in C_2H_4
Outlet of Gas Rich in CH_4

FIG. 76.—Claude coke oven gas separation plant.

forced through the column by means of a pump. The last traces of benzol are thereby removed and the heavy oil is then treated for removal of the benzol before recirculation.

The benzol free gas then passes through a column irrigated by an ammoniacal solution. The carbon dioxide and the hydrogen sulphide are absorbed by the solution, enter into combination with the ammonia, and are then removed. The carbonated ammoniacal solution is regenerated in a plate column where the compounds formed are decomposed by the heat so that the carbon dioxide and hydrogen sulphide escape. The regenerated ammoniacal solution is then re-circulated. In a third column the last traces of ammonia are removed by washing the gas with water.

The final column of the purification train is used for the removal of the last traces of carbon dioxide by washing with caustic soda solution. The gas is then dried by passing it over solid caustic soda or simply by cooling it down in the first exchanger of the liquefaction apparatus, and is ready for the liquefaction process for the fractional separation of the remainder of the gas constituents.

The liquefaction apparatus is really a heat exchanger divided into several elements, and the final temperature attained is of the order of — 200° C.

The dried, compressed and purified gases circulate in counter current with the separated and expanded gases in the heat exchanger.

The gas, therefore, is cooled progressively, and the condensable fractions liquefy in turn, i.e. ethane and ethylene first, then methane, carbon monoxide and nitrogen and these liquids are continuously removed from the circuit whence they are extracted and expanded. They then circulate in counter current with the incoming compressed purified gas, to which they yield their cold, and themselves are heated and finally vaporised and gasified.

After removal of the above constituents from the original coke oven gas, only hydrogen remains together with quite small quantities of nitrogen and carbon monoxide.

This remaining gas is then subjected to extremely low temperatures which removes all but the last traces of carbon monoxide. The hydrogen thus obtained is either further washed under pressure with liquid nitrogen to obtain a still higher purity, or sent directly to the expansion engine, where in expanding it performs useful work and is therefore cooled : it is this cooled expanded hydrogen which is used to reduce the compressed gases to the very low temperature (— 200° C.). Passing in counter current to the compressed gases, the hydrogen leaves the liquefaction plant at a temperature but little below that of the atmosphere.

The original coke oven gas is thus separated into its numerous constituents, and by special devices all these can be collected separately if desired for special uses.

For example, at Bethune ethylene obtained in the above manner is used in the synthesis of ethyl alcohol by absorption under moderate pressure in concentrated sulphuric acid and subsequent saponification of the ethyl hydrogen sulphate thus obtained. In 1930 this process at Bethune was producing over 1000 gals. of ethyl alcohol per day, and a similar installation with an output of 2500 gals. per day is now in operation at Ougrée Marihaye in Belgium.

Methane is also obtainable in quantity by the above Claude coke oven gas process, and since this can be obtained quite pure, it is suitable for conversion into useful products, i.e. by oxidation or transformation into unsaturated hydrocarbons, the properties of which are such that they are readily transformable into many useful chemical products.

To return to the pure hydrogen obtained from the coke oven gas, this is by this time ready for use in the ammonia process. In treating gases other than coke oven gas for the production of pure hydrogen, e.g. water gas, some slight modifications are introduced. In the case of water gas, the benzol removal column in which heavy oil is used for scrubbing can be eliminated, and the liquefying apparatus is simplified by omission of the ethylene and methane separation stages.

Hydrogen from Coke Oven Gas for Mont Cenis Ammonia Process.

The Mont Cenis synthetic ammonia process (which has been developed by the Gasverarbeitungs Gesellschaft of Westphalia, in conjunction with the Linde Eismaschinen Ges. of Munich) employs the Linde process for the production of hydrogen from coke oven gas, and the process is as follows :—

After being freed from tar, ammonia, benzol and sulphur in the ordinary way, the coke oven gas is compressed to 12 atmospheres. The average composition of such gas is as follows :—

	Per cent.
Hydrogen	50
Methane	22–24
Carbon monoxide	6
Unsaturated hydrocarbons . . .	2½
Carbon dioxide	3–4
Oxygen	1
Nitrogen	16

The compressed coke oven gas is freed from carbon dioxide by washing with high-pressure water and finally with caustic soda. It is then separated by successive liquefaction by the Linde process into its various constituents, and finally pure hydrogen is obtained. The Linde process differs from the Claude, in that the former uses the Joule-Thomson self-intensive cooling effect, whereas the latter uses an expansion engine to produce the cold necessary to liquefy constituents such as carbon monoxide. In the Linde process the last traces of carbon monoxide are washed out by spraying the gases at a temperature of — 190° C., with liquid nitrogen. This liquid nitrogen is obtained by compressing nitrogen to 150 atms. and then liquefying it by means of the Joule-Thomson effect. During the washing of the coke oven gas to remove carbon monoxide, part of the liquid nitrogen used for this purpose evaporates and forms, by mixing with the hydrogen thus purified, a mixture of nitrogen and hydrogen which by regulation of the addition of nitrogen is in correct proportion for the subsequent synthesis of ammonia.

The fractions of the coke oven gas separated by liquefaction, and which consist principally of an acetylene fraction, a methane fraction and a carbon monoxide fraction, can be either collected separately, or sent to one gasholder. This gas, which contains all the calorific value of the original coke oven gas less the hydrogen taken for the synthesis plant, can be used for the manufacture of additional hydrogen by means of thermal cracking of the hydrocarbons.

The nitrogen for the Mont Cenis plant is obtained from the liquefaction of air by the Linde process.

THE MANUFACTURE OF HYDROGEN FROM COKE OVEN GAS FOR THE SYNTHETIC AMMONIA PLANT AT OSTEND (LINDE PROCESS).

The Casale synthetic ammonia plant at Ostend, Belgium, also uses the Linde type of plant for the manufacture of coke oven gas, and I am indebted to the Union Chimique Belge for the following very complete description of this plant which was communicated by Dr. Pallemaerts of that company to the International Conference on Bituminous Coal (Pittsburg) in 1928.

This plant was the first to combine the Linde system of coke oven gas fractionation and the Casale synthetic ammonia process.

A special process had to be developed to purify the coke oven gas in view of its use for liquefaction, and it was found necessary to make slight alterations in the liquefaction process itself during the early stages of the operation of the plant. Considerable success was secured after these changes were effected, and the plant is now producing ammonia regularly at very low cost.

Extension of this Type of Ammonia Plant.

As yet (1928) the production capacity of plants of this type does not exceed 136 tons of ammonia per day, because gas is not available from existing coke oven plants in sufficient quantity to give larger outputs, and distillation works have not yet been systematically concentrated in Europe. However, a move is being made in this direction in Belgium, where a series of central carbonisation plants is being planned, arranged for generation of power and utilisation of gaseous by-products. The first of these central coking plants is to be erected in the southern Belgian coal field (Borinage) and will comprise a synthetic ammonia plant by the U.C.B. Linde-Casale systems, the first section of which has a capacity for 72 tons of ammonia a day. It is expected that a second central plant in Hainaut, Belgium, will be completed at about the same time.

Low Cost Due to Use of Coke Oven Gas.

Because of special conditions, it has been decided to instal, in addition to the coke ovens, a water-gas plant at Ostend on a scale sufficient for the production of 10 tons of ammonia per day. The reason is that the Ostend coke oven plant supplies gas to the town, which has large fluctuations in demand, being a seaside resort with a seasonal population.

The following costs are found for 1 cu. metre of hydrogen from different sources, under Belgian conditions, excluding the cost of extraction of the hydrogen from its gaseous primary material :—

	Belgian Francs.	*Dollars.*
In water gas :		
From coke at 170 Belgian francs per ton . .	0.22442	0.0062
From coal at 188 Belgian francs per ton . .	0.214	0.0059
In coke oven gas, at 0.14 Belgian franc per cubic metre, residual gas being valued at same price per calorie as original gas.	0.084	0.00234

Size of Plant.

The original Ostend plant, which was really experimental as it constituted the first application of the combined Casale-Linde-U.C.B. systems, was built for an output of 16 tons of ammonia per day. It comprised three 8-ton Casale units and three corresponding Linde units, one unit of each plant being in reserve.

For the first few weeks of operation the production was low and irregular, and improvements, bearing almost entirely on the purification of the coke oven gas preliminary to its fractionation, had to be made. Thereafter the production rose steadily until it reached an average of 18 tons, with peaks of 23 tons, giving a regular output 50 per cent. above that for which the plant was intended. Four additional Casale units have since been installed, and the hydrogen plant has been increased by two large units, each with a capacity of 3000 cu. metres of hydrogen-nitrogen gas; with these the plant produces 40 to 55 tons of ammonia per day.

A plant of this size is small compared with the I.G. plant, the Billingham plant of Imperial Chemical Industries in England, or the Hopewell plant of the Allied Chemical and Dyes Corporation now nearing completion. However, it is proportional to the size of the country, and, as already said, this type of plant especially lends itself to distribution and to economic operation under the conditions found in Europe. When coke oven plants have been concentrated as is now being planned, additional units will be added and favourable results are expected from the enlarged plants.

Thanks to the cheapness of the hydrogen, and also to the general economy of the Casale synthesis process, ammonia can be produced at the cost of about 9 American cents per kilogram of nitrogen in the form of ammonium sulphate (including the cost of the sulphuric acid and total operation costs, amortisation, etc.).

Genesis of the Type.

After the Semet-Solvay & Piette Company (which has since become a division of the Union Chimique Belge) decided to manufacture synthetic ammonia, the first problem was a cheap source of hydrogen. Coke oven gas was chosen for the reasons already given.

The next question was how to obtain hydrogen from this source. Several processes were investigated—fractionation and the iron-steam processes.

The last-named processes, which were being worked at the time by Bamag and by the Alais, Froges et Camargue Company, were carefully compared and the conclusion reached that the Alais process, which was conducted in batteries of externally heated retorts, had not been sufficiently improved. The Bamag or Messerschmidt system had been tried out on an industrial scale, but was found to require a large number of converters of small capacity, considerable labour, and to yield a rather impure hydrogen gas with a low-value residual power gas. So these processes were eliminated.

Of the fractionation processes, two were taken under consideration, both elaborated by world-famous firms; they were the Claude system and the Linde system. For certain reasons, the Linde process was finally chosen, and the Casale system was adopted after a careful study of the three then available synthetic ammonia processes.

Preliminary Treatment of Coke Oven Gas.

Such little experience as was available came from a small experimental plant situated at Oberhausen in the Ruhr district, where it had been installed with the collaboration of the Linde Company, by the originator of the coke oven gas hydrogen idea, Mr. Bronn, an engineer of the Rombacher Eisenhutten Company.

All that was known from the Oberhausen experience was that the gas had to be dry and free from carbon dioxide ; also that it probably would have to be desulphurised before compression. These conditions had been effected at Oberhausen through purification of the gas in iron oxide purifiers, followed by compression, washing under pressure with water to remove carbon dioxide, a final decarbonation by means of caustic soda, and drying under pressure by means of calcium chloride.

This treatment was not considered very practical for quantity production and it was proposed to replace both desulphurisation and decarbonation by an ammonia wash process, working under ordinary pressure. This was accomplished only after certain obstacles had been overcome, for the washing of gas with ammonia proved more difficult than might have been expected. The results of this treatment were excellent, the acid constituents of the gas being removed to the extent that less than 0·1 per cent. carbon dioxide remained, which is better than is obtained with a pressure water wash, which leaves as a rule 0·3 to 0·4 per cent. carbon dioxide.

The chemical drying of the gas was omitted and left to the refrigerating plant.

The hydrogen plant was started up along these lines, but difficulties arose from the presence of heavy unsaturated hydrocarbons in the gas ; these hydrocarbons polymerised in the less cold parts of the hydrogen apparatus and caused obstructions and even local explosions. One apparatus was even partly destroyed, and, as a larger unit (3000 cu. metres of hydrogen-nitrogen) was under construction, the small unit was not rebuilt. A thorough investigation of the causes of the trouble was undertaken, and it was decided to instal a pressure water wash in order to remove all hydrocarbons which had a solubility coefficient higher than 1. This proved very effective, and the plant has been running smoothly ever since.

A few incidents of minor importance, however, have shown it desirable to carry the purification process still further, for the purpose of removing oxides of nitrogen and volatile nitro compounds. A simple physical treatment of the gas has been devised, of which excellent results are expected. The trouble due to the formation of explosive copper acetylide has also been eliminated.

The ammoniacal liquor obtained in the decarbonation treatment of the gas is distilled into the sulphate saturators. This simple process will be replaced in future plants by a system in which the ammonia is regenerated for the same purpose, in order to make all the liquid ammonia produced in the ammonia plant available for uses other than sulphate manufacture from sulphuric acid.

Lately, patent applications have been made for a process replacing the whole classical treatment of coke oven gas for the recovery of ammonia and benzene by a new simplified system combined with the synthesis of ammonia. Future coke oven plants built by U.C.B. will in all probability be without saturators or benzene scrubbers in their by-product department.

Plant for Manufacture of Hydrogen.

This plant was built entirely by the Linde Company.

The purified compressed gas is cooled in stages, first in a countercurrent cold exchanger, then in a liquid-ammonia refrigerator, and finally in the fractionation apparatus, where the Pictet cycle is applied, together with the Joule-Thomson effect on nitrogen. This fractionation apparatus is arranged to utilise in the most effective way the cold contained in the condensed gases that are tapped off at various points on the gas circuit as the temperature is lowered.

The condensates which are successfully removed are, in order :

(1) *Ethylene* at a temperature of about 120° A. This liquid, although called ethylene, contains only 20-30 per cent. of C_2H_4, the other gases being propylene, ethane, methane, and some uncondensed coke oven gas.

(2) *Methane* at temperatures of 25°-85° A. ; it contains mainly methane, with ethane, ethylene, and uncondensed gas.

(3) *Carbon Monoxide*, a liquid mixture of carbon monoxide and nitrogen, with some methane, ethylene, etc.

The compressed cold gas that is left is now a mixture of hydrogen and nitrogen, but still contains small quantities of methane and carbon monoxide. These impurities are almost totally eliminated by means of a liquid nitrogen wash, which removes methane entirely and leaves only 0·001 per cent. of carbon monoxide. Oxygen and water vapour are also totally removed.

Cost of Linde Coke Oven Gas Hydrogen.

The two main factors in the cost of Linde coke oven gas hydrogen are energy and the cost of the coke oven gas itself. The energy consumption per cu. metre of hydrogen at atmospheric pressure is 0·246 K.W.H. The total expenses for the production of 1 cu. metre of hydrogen (without nitrogen and at atmospheric pressure) amount to 0.141 Belgian franc ($0.00395). The cost of the coke oven gas which is used obviously depends on the available market or on the assumption made as to its value. In certain cases, where there is no sale for coke oven gas and where its cost is taken as the difference between coal plus operation expenses and total income from by-products, it may be considered as having little or no value. This is unusual, however, and is daily becoming more so.

At the Ostend plant, where gas is sold to the city gas distribution company at the same price per kilogram-calorie as coal, the cost of gas is as follows :—

2·3 cu. metres of coke oven gas at 0.14 Belgian franc per cu. metre = 0.323 Belgian franc.

However, as the Linde process returns 70 per cent. of the calorific power of the gas in the form of a high-calorific-power gas at 6500 to 8000 kilogram-calories per cu. metre ; and when allowance is made for the income from this source. counting the hydrogen-free gas at the same price per kilogram-calorie as the original coke oven gas, the detail is as follows :—

$$30/100 \times 0.323 = 0.0969 \text{ Belgian franc } (\$0.0027).$$

The total cost of Linde coke oven gas hydrogen is therefore 0.00395 + 0.0027 = $0.00665 per cu. metre ($0.1883 per 1000 cu. ft.).

Utilisation of Residual Gas.

In this calculation the residual high-power gas, which consists mainly of methane and ethylene and their homologues, with some nitrogen, has not been valued at more than the original coke oven gas per calorie. This is a fair assumption as long as it is not used for any other purpose than coke oven gas itself is used. But this gas is much more valuable than coke oven gas. In the first place, it is entirely free of all sulphur compounds and other impurities, and is absolutely anhydrous. It also is particularly suited for certain industrial uses, such as the heating of special furnaces—the Libbey-Owens process for instance—and it also lends itself remarkably well to long-distance conveyance of gas which is being developed in continental Europe. A simple calculation shows that 1 million kilogram-calories represent 121 cu. metres of rich residual gas at 8270 kilogram-calories per cu. metre or 214 cu. metres of ordinary coke oven gas at 4680 kilogram-calories per cu. metre. The compression of these volumes to 30 atms., which is generally admitted as being suitable for long-distance distribution, will require 25·4 h.p. in the case of the former gas, as against 45 h.p. in the case of the latter. The energy economy will therefore be 43·5 per cent. in favour of residual gas.

The above advantages concern only the crude uses of the rich residual gas in the crude form. This gas, however, lends itself to even more valuable application, for its components can be collected separately and used in a whole series of chemical processes to form valuable products.

Ethylene can be converted into ethyl alcohol (this application has already been put into practice in certain European plants), diethyl sulphate, or any of the valuable halogen addition products. Propylene, which accompanies its lower homologue, can be transformed into its corresponding alcohol by the same process.

The Linde Company builds ethylene fractionating apparatus which will convert the 30 per cent. "ethylene" obtained in the ordinary Linde coke oven gas fractionating apparatus into 80-95 per cent. ethylene, the gas being thus rendered suitable for chemical processes requiring ethylene of high purity. The ordinary 30 per cent. ethylene can be used without rectification in many processes, especially in alcohol and ether manufacture.

A Linde ethylene fractionation apparatus has been installed by the I.G., and another will soon be working at the Ostend plant of the U.C.B.

Methane has not yet found any considerable industrial use, and it is merely used for heating purposes. A certain amount, however, is compressed into tubes and used for oxy-methane steel-cutting and for the soldering of steel, lead, etc. A small quantity of hydrogen has to be mixed with the methane in order to increase the velocity of combustion, which is too slow in the case of methane alone. This use will probably never absorb the entire production of methane in coke oven gas hydrogen plants ; but without doubt additional uses for methane will sooner or later be found, probably in the direction of its polymerisation into liquid hydrocarbons.

One utilisation of methane is already becoming industrial. It consists in cracking methane into hydrogen and carbon dioxide, by the action of steam and the use of suitable catalysts. This transformation, which at first may seem a degradation, is useful where a large quantity of hydrogen is required from a small quantity of coke oven gas. Indeed, whereas 1 volume of coke oven gas will yield 0·5 volume of hydrogen, the same quantity of coke oven gas will give 1·7 volumes of hydrogen, or more than three times as much, if methane is converted into hydrogen. It will therefore be apparent that the advantage is considerable, even without a remunerative use for methane.

It must not be forgotten, however, that in this case there is little residual gas left for heating the ovens, which have to be supplied with some other gas, such as producer gas, and this gas is usually more expensive per calorie than coke oven gas under European conditions.

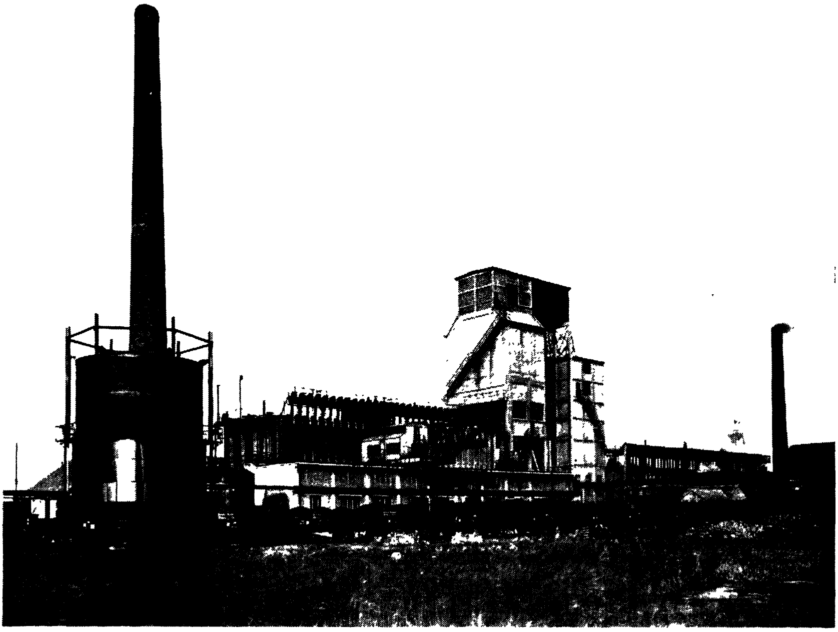


FIG. 77.—Coke oven plant. (U.C.B., Ostend, Belgium.)

[*See page* 123.

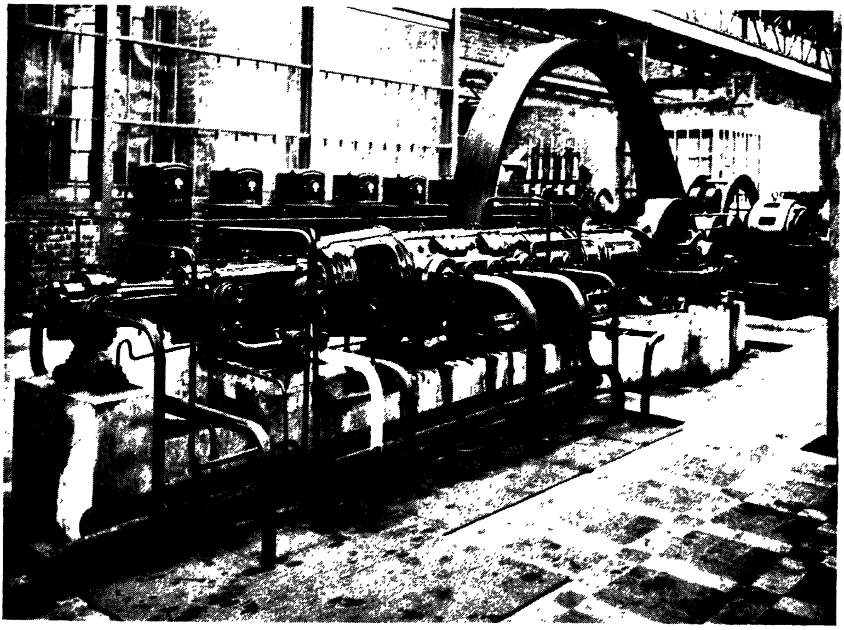


FIG. 78.—Nitrogen compressor. Synthetic ammonia plant. (U.C.B., Ostend, Belgium.)

[*See page* 125.

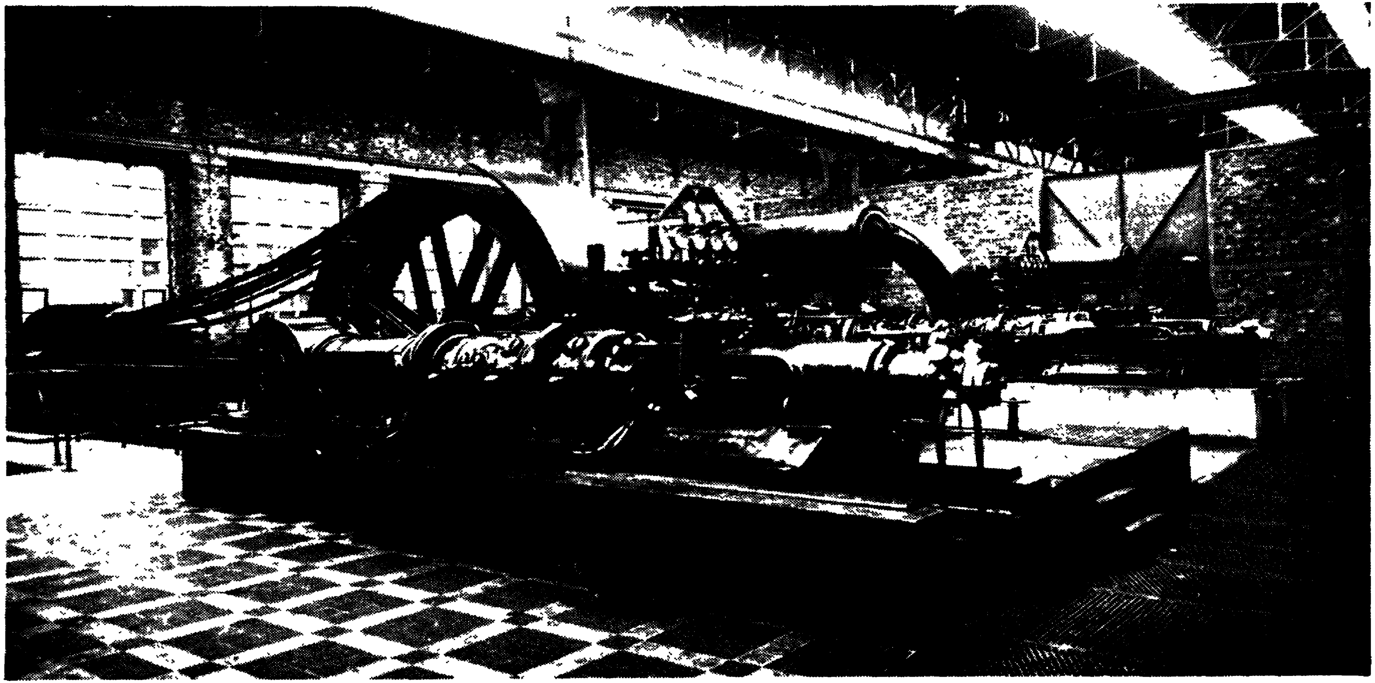


FIG. 79.—Compressor room Casale plant. (U.C.B., Ostend.)

[*To face page* 127.

It will be seen from the above that, based on the residual gas having the same value as the original coke oven gas, the price will probably be lowered considerably if the various constituents of the residual gas are exploited to the greatest possible advantage.

Description of Ostend Type of Coke Oven Hydrogen Plant.

Coke oven gas from the adjoining coking plant, which has undergone the usual treatment for by-product recovery, is extracted by means of exhausters and submitted to a treatment in which it is successively washed with an ammonia solution, with water in sufficient quantity to remove the ammonia carried over, then with sulphuric acid, which eliminates the last trace of ammonia, and finally with caustic soda, which fixes any sulphuric acid or carbonic acid which might be left in the gas.

The purified gas is stored in a gasholder, from which it is exhausted by compressors which compress it in two stages to about 9 atms. Under this pressure it is refrigerated by means of liquid ammonia from the synthesis plant, and in passing through a cold exchanger it is warmed again to about normal temperature.

At this temperature it is now washed with water in pressure water-wash towers, where 1 volume of compressed gas is washed with a little more than 1 volume of water. The older towers pass about 1750 cu. metres of gas per hour, the new towers about 5300 cu. metres, and the corresponding quantities of water.

The energy of the water as it leaves the pressure towers is recovered in hydraulic turbines placed on the same shaft as the pumps and motors, each group comprising motor, pump and turbine. The motor has to do all the work at the start, but its power consumption falls to about 40 per cent. when the water is admitted through the turbines.

This water evolves gas as soon as it has passed the turbine, like soda water in a bottle when the stopper is removed. This gas is collected and returned to the residual gas from the fractionation. The " degasification gas " is not all carbon dioxide, as in the case of the Haber-Bosch water wash, where a gas with 30 per cent. carbon dioxide is pressure-washed. Indeed, the gas here, besides containing originally only 1-2·5 per cent. carbon dioxide, has been very completely decarbonated in the ammonia wash. The object here is entirely different, and is to remove mainly acetylene present in the proportion of 4 parts per thousand only. It seems ridiculous to have to resort to such powerful means to remove a disagreeable gas present in such minute quantities, but the treatment is effective, besides being absolutely necessary, until some better means is brought into action. As it is, the " degasification gas " has the following composition :—

	Per cent.
Olefins	12
Oxygen	1
Carbon monoxide	6
Hydrogen	31
Methane	38
Ethane	2
Nitrogen	10

There is no use for this gas other than to incorporate it into the residual gas used for heating purposes.

The coke oven gas, which is now free from benzene and amply purified, is refrigerated for the second time by means of cold exchangers and ammonia refrigerators to a temperature of about —45° C. At this temperature water vapour is removed sufficiently to avoid rapid obstruction of the fractionating apparatus due to freezing of the condensed water. The gas now enters the fractionating apparatus, and leaves it in part as a pure mixture of hydrogen and nitrogen with the desired nitrogen percentage for the ammonia synthesis and in part as various " residual " gases which at present are mixed and, after cold exchange, return to the coking plant where the joint residual gas is used to heat the coke oven batteries.

These coke ovens, which are of the U.C.B. (Semet-Solvay & Piette) combined type, are arranged for heating by producer gas, rich gas, or any intermediate gas. The most varied gaseous mixtures, depending upon the demand for gas from the town gas-distribution company, which they also supply, are used successfully. Sometimes some coke oven gas is used, but the normal supply is a variable one consisting of producer gas (from U.C.B. automatic producers gasifying coke breeze) and rich residual Linde gas. The ovens work splendidly on this variable but well-controlled mixture. They have been working for nearly four years now under these conditions.

As previously mentioned, in the original plant no provision was made for the use of the water wash, and there was some trouble with the fractionation plant, when a large quantity of benzene was collected at the ammonia refrigerators. When the water-wash plant was started, there was no longer any benzene to be seen, proving that all the benzene was dissolved by the pressure water, which acted more effectively than any oil wash. It was therefore decided to instal a second refrigerator before the water wash, so that benzene was again recovered. This system of benzene recovery does not consume any energy or materials, as it consists simply of static refrigerators and cold exchangers and is run on liquid ammonia from the synthesis plant.

Since the Ostend plant has been started, the Linde Company has built a number of installations, treating daily a total of more than 2·5 million cu. metres of coke oven gas. Besides the extensions to these various plants under preparation, or already being carried out, as at Ostend, several large new installations have been planned. The earliest plants, except for the experimental unit at Oberhausen, were built first in Belgium and then in France, but of late several large ones have been erected in Germany. It now looks as if the Germans, who apparently were at first content to rely on the I.G. process, are seriously entering the field with the Linde coke oven gas hydrogen process.

In all, the Linde Company (1928) has provided 7 units of 1600 cu. metres of coke oven gas per hour, and 19 units of 5000 cu. metres per hour—all for ammonia synthesis. One unit for treating 7500 cu. metres of gas per hour is under construction, which will supply hydrogen for the Bergius process.

It is worthy of notice that the Linde hydrogen-nitrogen process does away with the expensive combustion of hydrogen in air, which is applied in certain plants in order to incorporate the necessary amount of nitrogen into the gaseous mixture. Linde nitrogen costs in power only 0·2 K.W.H. per cu. metre in the larger unit, and it would be necessary to secure hydrogen for nothing in order to justify using 1 volume of precious hydrogen in order to obtain 2 volumes of nitrogen.

In the hydrogen-nitrogen apparatus the nitrogen, besides coming partly from the coke oven gas itself, is introduced by saturation of the hydrogen with nitrogen during the liquid nitrogen wash. The nitrogen proportion is ingeniously regulated by acting on the temperature of the gas, the pressure being kept constant. The temperature itself is regulated by the pressure under which liquid nitrogen is kept in the liquid nitrogen boiler, which constitutes the last stage in the cooling of the gas.

A pressure of about 0·2 atm. in the nitrogen boiler ensures the required nitrogen percentage in the mixture, the gas itself being under 9 atms.

It has been found useful at Ostend to generate hydrogen with a little less than 25 per cent. of nitrogen, and to correct the mixture in each synthesis unit by means of an addition of nitrogen.

The Ostend nitrogen machines are of a size corresponding to the hydrogen units. They produce pure nitrogen of 99·8 per cent. purity and at the same time pure oxygen at 99 per cent. The Linde Company builds units much larger than those at Ostend, the largest making 3600 cu. metres of nitrogen per hour (126,000 cu. ft. per hour). In one plant 16,000 cu. metres (560,000 cu. ft.) of nitrogen are produced per hour.

Manufacture of Rare Gases by Pressure Processes.

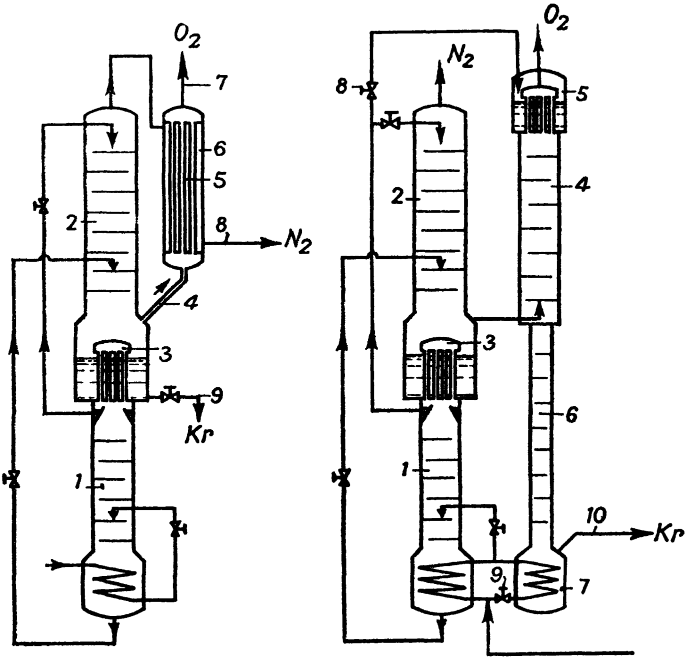
Many of the rare gases are now obtained by pressure processes. A case in point is the rare gas neon, which is used in the well-known "neon lighting" system of illumination, and is obtained by the liquefaction of air and the subsequent separation of neon (and also helium) from the nitrogen fraction (Georges Claude, "Conferences de M. Georges Claude, University of Brussels," *Bulletin de la Société Belge des Ingenieurs et des Industriels*, 1924). By quite a minor alteration in the Claude fractionation column, it is possible—from an air separation plant producing 200 cu. metres of oxygen per hour—to obtain 700 litres per day of a mixture containing 55 per cent. of neon; the remaining part (45 per cent.) is composed of about two-fifths of helium and three-fifths of nitrogen; Claude found that there are three parts of neon and one part of helium in 200,000 of air.

Claude and the Linde organisations have also endeavoured with characteristic energy and ingenuity to obtain krypton and xenon from gaseous oxygen plants, but the quantities are, of course, extremely small (*Compte Rendus*, 1928, **187**, 581). From a gaseous oxygen plant treating 800 cu. metres of air per hour, Claude was able to obtain 10-11 litres of krypton and about 1 litre of xenon per day by special treatment of the "oxygen bath" of the fractionating column of the liquid air plant.

A recent English patent (No. 390069, March, 1933) granted to the Linde Eismachinen A.G. for the commercial production of krypton and xenon from liquid air plants is of interest in this connection. The following is a brief abstract of the examples given in the patent specification, and the text will be clarified by reference to Fig. 80, which shows details of the invention.

In Fig. 80 (I), the pressure column is indicated by 1; 2 shows the upper column, and 3 the evaporating vessel with condenser of an air decomposing apparatus. The gaseous oxygen, containing krypton, which leaves the evaporating vessel at 4, is led into the vertical tube assembly 5, through whose cover tube 6 flows the cold gaseous nitrogen produced, which passes out at 8. As the nitrogen is 13° colder than the oxygen, and as its amount is some four times the amount of the oxygen, a copious concentration of oxygen takes place in the upper part of 5. The liquid flowing back in the opposite direction to the gas stream washes the krypton out of the rising gaseous oxygen, becoming thereby, for the greater part, vaporised again, and the liquid residue thus enriched in krypton. As the gaseous oxygen reaching the upper part of the tube assembly is freed from krypton by the washing described, it is thus possible to produce, with the arrangement described, a krypton-free washing liquid in the upper part of the condenser. The washing liquid containing krypton flows through 4, back into the evaporating vessel 3; a further progressive concentration of the krypton takes place there. At the end of the working period of the decomposing apparatus, the liquid of the evaporating vessel, containing practically the whole of the krypton in the air treated, is drawn off at 9 and worked for pure krypton in a known manner.

With the method of working shown in Fig. 80 (II) the washing and concentration of the krypton takes place in the rectifying columns.



(I.) (II.)

FIG. 80.—Linde process for recovery of krypton and xenon from air separation plants. (See pages 100-105 for details of principles of air separation apparatus.)

The krypton-containing oxygen coming from the evaporating vessel 3 of the decomposing apparatus is led into the washing column 4, which is provided with rectifying trays. The condensation of the krypton-free washing liquid takes place here in the condenser 5 carried on 4, and which is cooled with liquid nitrogen. This is brought in through the valve 8. The action of the column 4 corresponds in principle with the action already described of the tube assembly 5 (Fig. 80 (I)). The liquid oxygen contained in the krypton arriving at the foot of column 4 is passed on to the concentrating column 6 and there further concentrated. This column is heated by means of compressed air, whose quantity is regulated by the valve 9. The highly concentrated krypton can be drawn off in gaseous form at 10 from the evaporating vessel 7, or it may be drawn off in a liquid condition. With this last described method of working it is possible to obtain the krypton in a continuous stream and in any desired concentration.

(NOTE.—A small quantity of xenon is recovered with the krypton.)

As previously stated helium is obtainable from oxygen plants, but the quantity is again small. Claude & Linde air separation plants are capable of producing it with very little alteration to the oxygen-nitrogen fractionation column by extracting it from the mixture neon-helium-nitrogen. The quantity obtained is about one-third that of the neon obtained at the same time.

Natural gas wells in U.S.A. and Canada are the most prolific sources of helium at the present time, as the gases contain from ½ to 2 per cent. of this gas.

The biggest plant for the commercial production of helium is at Amarillo, Texas. The plant is on the site of a large natural gas territory, wherein the helium content is as high as 2 per cent. The plant is operated and run by the Bureau of Mines of the U.S. Government. The carbon dioxide content of the original natural gas is removed by washing with caustic soda, and the other constituents are then separated by fractionation at low temperatures. The helium is purified to give 98 per cent. purity, and is then compressed into large cylinders for storage purposes at pressures of 130 atms. The storage capacity of the plant is 3,000,000 cu. ft. of helium (measured at N.T.P.).

Use of Compressed Town's Gas as a Fuel for Internal Combustion Engine Driven Vehicles.

Pressure is playing an important rôle in the employment of town's gas as a fuel for internal combustion engine driven vehicles, and an abstract of the paper, " The Development of the Use of Gas as a Substitute for Petrol for the Propulsion of Heavy Vehicles," which was read by Dr. C. M. Walter before the recent World Pretoleum Congress is of interest in this respect :—

The use of town's gas as a fuel for high-speed internal-combustion engines dates back to pre-war days, when, as at present, large quantities of town's gas were used for the " running in " of high-speed engines primarily designed for running on petrol.

In those days the compression pressures used in engines of this type were comparatively low, with the result that when running on town's gas, the maximum power developed did not reach that obtained with petrol.

During the period of the war, many types of vehicles were run on gas, owing to the shortage of petrol, the gas being stored in the majority of cases in large flexible bags, usually housed on the roof of the vehicle, and where the compression ratios of the engines were reasonably high, the thermal efficiencies realised were of a high order.

The main difficulty which presented itself, however, was the somewhat limited capacity of fuel storage, which resulted in the radius of action of the vehicle being somewhat restricted.

At that time the possibility of storing gas in the compressed form in steel cylinders was given serious consideration, but it was found that this scheme was impracticable owing to the weight of the containers being too great in comparison with the amount of gas stored.

Since 1927, however, a considerable amount of research work has been done in connection with the manufacture and use of high-tensile alloy steel bottles, made from nickel, nickel-chrome or nickel-chrome-molybdenum steels, and in view of the possibility of steel bottles of this type overcoming to a considerable extent the difficulties of storage referred to, and thus enabling a vehicle to cover a reasonable distance on a single charge, the Birmingham Gas Committee decided to fully investigate the matter.

Since December, 1931, very complete investigations have been made in connection with the use of bottles of this type for the storage of gas on vehicles, and further, a good deal of experimental work has been done on the running of engines on gas in place of petrol, with a view to determining to what extent the designs might have to be modified to obtain the most efficient results.

The investigations referred to above, which were carried out in the Industrial Research Laboratories of the City of Birmingham Gas Department, culminated in two vehicles being placed on the road, operating on gas. One is a 20 h.p. Austin delivery van, which has now been operating since October entirely on gas as a fuel, giving extremely satisfactory results. The other is the 32-seater 'bus which has been running on ordinary service work in Birmingham since February last.

The results of tests carried out with these two vehicles seem to show quite definitely that 265 cubic feet of 475 B.Th.U. gas give the same performance as 1 gallon of petrol, provided that certain alterations to the engines, such as increasing the compression ratios and modifying the ignition gear, are made.

In the case of the 20-horse van, five light-weight cylinders, each containing 354 cubic feet of gas at 3000 lbs. per sq. in., enable the vehicle to operate over a distance of 85-100 miles per charge, whilst in the case of the passenger 'bus, which is fitted with seven similar cylinders, the gas consumption per mile varies from 50 to 70 cubic feet, according to the particular routes on which it is running ; thus, approximately 50 miles can be run on a single charge.

Whilst it is recognised that this might be a disadvantage, in so far that passenger vehicles running upwards of 100 miles per day might have to completely re-charge or " top-up " en route, in view of the limited range of action per charge as compared with petrol, it would appear that these difficulties are by no means insuperable, and it is anticipated that at an early date, quick acting union connections will be utilised for making the connection of the vehicle to the charging station, and by the employment of storage cylinders, storing gas at pressures of upwards of 5000 lbs. per sq. in., the time required for filling would be reduced to a minimum.

It is anticipated that with suitable arrangements, a vehicle could " top-up " in approximately 2½ mins. and completely charge in 3½ mins., whereas at present, the time taken is almost double this figure.

With regard to the cost of compressing gas to a pressure of 5000 lbs., it is found that approximately 11 h.p. hours are required for each 1000 cubic feet of gas, compressed and delivered at 5000 lbs. per sq. in., this latter pressure being that at which gas is stored in the storage bottles for filling the working bottles on the vehicles to a pressure of 3000 lbs. per sq. in.

Compressors of the four- or six-stage type are used for this purpose and may be either direct coupled to steam engines or electric motors, the steam-driven set, perhaps, being the most flexible unit for the purpose.

A steam-driven compressor, driven by a compound condensing engine, approximately 220 h.p., would be required for a delivery of 20,000 cubic feet of compressed gas per hour, at a delivery pressure of 5000 lbs. per sq. in.

If steam can be obtained at 1s. 10d. per 1000 lbs. or electricity at 0·48d. per unit, the cost of compressing would amount to about 13d. per 1000 cubic feet, this figure including capital and depreciation charges on plant in addition to energy costs.

From actual road tests, as previously mentioned, it is found that 265 cubic feet of gas of calorific value 475 B.Th.U.s gross give the same performance as 1 gallon of petrol. Thus, with gas of this calorific value at 4d. per therm, the total cost would be 1s. 7d. per 1000 for gas plus 13d. for compressing = 2s. 8d. per 1000.

Taking 265 cubic feet of gas equal to 1 gallon petrol, the cost per equivalent gallon of petrol would be 8·48d., this not including any capital charges on the vehicle equipment itself.

In addition to the saving which can be effected in fuel cost of running, it is found that the wear and tear of the engine is reduced when operating on gas as compared with petrol, and the cost of maintenance is thus considerably reduced.

Compression and Storage Plant.

During the period of experimental work on engines, further experimental work was being conducted in connection with the design of multi-stage compressors, storage cylinders required to store gas at the filling station for charging vehicle cylinders, and light-weight cylinders suitable for mounting on vehicles for storing gas at working pressures up to 3000 lbs. per sq. in.

A considerable amount of information has already been published in regard to the various qualities of steels employed for the production of storage cylinders of this type, but it might be of interest to point out that at the present time most of the cylinders used on actual vehicles are composed of alloy steels containing nickel, chromium and molybdenum.

The dimensions of these cylinders approximate to 8 ins. outside diameter and 73 ins. long, with a wall thickness of 0·22 in. The internal volume is 1·76 cubic feet, and thus at a working pressure of 200 atms. the volume of free gas contained is about 352 cubic feet, and the approximate weight of each bottle empty is 119 lbs. The number of bottles carried depends on the size and type of vehicle.

Alloy steel bottles of this type are being manufactured by Vickers-Armstrong Ltd., Newcastle-on-Tyne, and the Chesterfield Tube Company. In the case of a test specimen from a bottle made by the former firm, the following results were obtained :—

Ultimate strength .	67·9 tons per sq. in.
Yield . . .	59·5 ,, ,, ,,
Impact . . .	53·0 ft.-lbs.
Elongation . .	22·8 per cent.
Reduction of area .	59 ,,

Bending Test : Bent through an angle of 180° without cracking. Limit of proportionality, i.e. maximum stress at which strain is proportional to load, 47 tons per sq. in.

In the case of vehicle bottles with a working pressure of 3000 lbs. per sq. in., the wall thickness is such that the maximum working stress is 25 tons per sq. in., whilst in the case of the stationary storage cylinders where a working pressure of 5000 lbs. per sq. in. is employed, it is proposed that a working stress of not more than 16·7 tons per sq. in. should be employed, this giving a factor of safety of three in the case of cylinders heat-treated to give an ultimate strength of 50 tons per sq. in.

Vehicle Equipment.

The complete equipment necessary to operate a vehicle on town's gas includes :—

A battery of storage cylinders of the type already described, suitably attached to the chassis frame and interconnected by means of solid drawn steel pipes fitted with suitable valves of forged steel.

The number of storage cylinders employed will, of course, depend on the type and weight of vehicle, and the mileage required from a single charge.

Further, a suitable reducing valve to reduce the pressure from the working pressure in the storage cylinders to any desired pressure at the engine inlet, is required, in addition to an air-gas mixer which takes the place of the ordinary carburettor.

The usual form of reducing valve employed consists of a two-stage diaphragm type, so designed as to reduce the pressure from, say, 3000 lbs. per sq. in. to 5 lbs. per sq. in. in the first stage, and from 5 lbs. per sq. in. to any pressure that may be required at the air-gas mixer, in the second stage.

The valve areas are such that at all loads the requisite flow of gas into the induction system is maintained.

With the system at present employed on the vehicles referred to, the pressure of the gas is reduced to sub-atmospheric in the second stage of the reducing valve, in order to ensure that when the engine is stationary, the supply of fuel is automatically cut off, as the second stage valve will only operate when under the influence of the depression caused in the induction system by the engine suction. As will be seen later, however, it might be desirable with certain designs of engines to arrange for the gas to be supplied at a slight positive pressure, in order to maintain a high volumetric efficiency over a wide range of loads. In the latter case, the gas and air required would be admitted to the cylinders through independent valves, and not as an admixture, as is the case where air-gas mixers of the type referred to below are employed.

With regard to air-gas mixers, the results of experimental work carried out with engines on bench tests and also on vehicles running under service conditions, would seem to indicate that when the gas and air are admitted to the induction system by means of a choke, the most satisfactory way of obtaining the best admixture of air and gas is to reduce the gas pressure to atmospheric pressure or slightly below and to depend on the suction of the engine to cause both air and gas to be induced into a choke tube of suitable dimensions, where intimate mixing takes place. In the case of certain designs of engines, it has also been found to be advantageous to introduce velocity tubes in the induction manifold to further assist admixture of gas and air by bringing them more into intimate contact.

The type of mixer at present employed consists of a Venturi choke tube through which the air is drawn, the gas entering through ports, in the form of slots, arranged at right angles to the air stream, these ports being suitably placed circumferentially around the contracted section of the choke tube itself.

The advantage of being able to ensure a constant air-gas ratio over a wide range of speeds with this simple type of mixer will be apparent, as the volume of gas and air induced into the induction system will follow closely the square root law, the proportion of air to gas thus remaining constant over a wide range of throttle opening.

Gas Compression Plant.

In order that minimum power is required for driving the compressor, the isothermal efficiency, which may be defined as the ratio of the theoretical isothermal horse-power to the actual horse-power, should be as high as possible. For four- and six-stage machines, the power required is approximately 11 h.p. hours per 1000 cubic feet of gas compressed and delivered at 5000 lbs. per sq. in.

The experimental compressor employed was manufactured by Messrs. Belliss & Morcom and is a four-stage machine. It is designed to compress and deliver 10 cubic feet of gas per minute at 5000 lbs. per sq. in. The gas passes through intercoolers after each stage, which ensures a high isothermal efficiency.

The machine is of two-crank design with three compression stages on each line, that is, first, second, and third compression stages on one line and first, second and fourth compression stages on the other line. The two first stages discharge into the respective second stages and the two second stages into the common receiver coil for the third stage, then from the third to the fourth stage. Each stage is fitted with a relief valve which is piped to atmosphere.

All moving parts are under forced lubrication, and it has been found that, providing the lubrication is adequate, there is no trouble from the point of view of wear of the moving parts in the higher stages.

At the present time, a further six-stage machine is being installed at one of the works of the Birmingham Gas Department, with a view to increasing the facilities for supplying gas for vehicles at pressures of 3000 lbs. per sq. in. This machine will be capable of delivering 100 cubic feet of free gas per minute into storage cylinders at a pressure of 5000 lbs. per sq. in., from which vehicles will be filled to a working pressure of 3000 lbs. per sq. in.

The machine will be steam-driven by means of a compound condensing engine of about 65 B.H.P., and it is estimated that the cost of compressing, including all charges, will approximate 13d. per 1000 cubic feet.

The method of charging the storage cylinders is by means of a pipe line, in which are inserted suitable relief valves at different points, in order to prevent any possibility of over-charging.

Conclusions.

From the results of the experimental work which has been carried out in Birmingham up to the present time, there seems little doubt that town's gas can be employed with distinct advantage as a substitute for petrol, particularly in the case of the heavier types of vehicles, the advantages to be obtained resulting in reduced running costs where gas can be obtained at round about 4d. per therm, and also to considerably increased flexibility, which has been so pronounced in the case of all engines so far experimented with.

Further, it is found that engines, after being suitably modified to run on town's gas, will run at idling speeds considerably below those which are obtainable with petrol, and the completeness with which combustion takes place over a very wide range of power output is indicated by the fact that over the range of full load to idling, no carbon monoxide is found to be present in the exhaust.

It will be appreciated from what has been said that, so far, the experimental work which has been carried out has been connected with engines primarily designed to run on petrol, with certain modifications such as increase of compression ratio, to enable reasonable thermal efficiencies to be realised, but there seems little doubt that it would be possible from the experience now obtained to design engines for running on town's gas, which would show very considerable increases of efficiency over those obtained up to the present.

Dr. C. M. Walter particularly wishes to refer to the possibility of the application of town's gas to an engine designed for fuel injection, somewhat similar to the principle at present used in the Diesel engine, and to the very high efficiencies which can be predicted as possible of accomplishment from engines of this type as compared with the standard design of unit.

The ordinary type of petrol engine operates on what may be considered a constant-quality variable-quantity cycle ; that is to say, during the induction stroke, the quantity of charge is increased or reduced according as the throttle is opened or closed, the quality of mixture being more or less constant. This results in the average volumetric efficiency being very low, as it will be appreciated that whilst the volumetric efficiency might be as high as 85 per cent. when working under full load conditions, it would fall to practically zero when the throttle opening is reduced for idling purposes.

If we consider the case of an engine working on a constant-quantity variable-quality cycle, so arranged that during the induction system a full charge of air is taken into the working cylinder, the fuel being added in proportion to the load at a certain point in the compression stroke, we shall find that under widely varying conditions of load, the volumetric efficiency remains very nearly constant, with the result that very high thermal efficiencies will be obtained over a wide range of speed and power outputs.

With an engine working in this manner, it is quite possible that an average brake thermal efficiency approximating to 30 per cent. might be obtained under normal working conditions, that is, even at a comparatively low load factor, as compared with a figure of 13-15 per cent. which might represent the average figure obtained with present designs of engines when running under average conditions. This would mean that the fuel consumption would be reduced by approximately 40 per cent., which would, in turn, result in the radius of action for a given charge being considerably increased.

Recent British Patents dealing with the Production of Industrial Hydrogen.

The following recent British patents are included to show the trend of development in the manufacture of hydrogen, and nearly all deal with the subject from the point of view of the production of this gas from coke oven gas, water gas, or hydrocarbons.

Removal of Carbon Monoxide and Dioxide, etc., from Gas Mixtures containing Hydrogen.

246,168. *Removal of carbon monoxide from the nitrogen-hydrogen mixture for the synthesis of ammonia.*

Soc. L'Air Liquide. 1925.

The carbon monoxide content of a gaseous mixture is converted into alkali or alkaline earth formate by absorption in concentrated alkaline solution under a pressure of 300 atms., or over, and at a temperature of the order of 400° C. The gases and alkali solution flow in counter current through the absorption chamber. The inner gas contact parts of the chamber are preferably copper covered to prevent undesirable decomposition of the carbon monoxide into carbon dioxide and carbon.

258,887. *Removal of carbon monoxide from gaseous mixtures containing hydrogen.*

Lazote Inc. September, 1925.

Carbon monoxide is removed from hydrogen-containing gases to be used in the synthesis of ammonia by passing under pressure over a catalyst capable of forming oxygenated compounds, such as methyl alcohol, and then removing the latter by condensation whilst the gases are still under pressure. Preferably the pressure is that under which the resulting hydrogen-containing gas is to react.

271,852. *Removal of carbon dioxide from gas mixtures.*

I.G. Farbenindustrie, A.G. May, 1926.

Carbon dioxide is removed from gases such as the crude mixture to be used in the synthetic manufacture of ammonia by washing with aqueous ammonia in a series of scrubbing towers. The towers may contain packing material such as Raschig rings, supported on grids. Final traces of ammonia are removed from the gases by scrubbing with sulphuric acid in a final tower.

341,748. *Removing carbon dioxide from gases.*

Naamlooze Vennootschap de Bataafsche Petroleum Maatschappij. February, 1930.

Carbon dioxide is removed from gases containing it (such as those obtained in preparing hydrogen from hydrocarbons such as methane by incomplete combustion or reaction with steam) by passing the gases mixed with steam in excess and at ordinary or increased pressure over sodium or potassium carbonate heated to a temperature above the condensing point of steam.

Alkali bicarbonate is formed, and may be heated to regenerate the carbonate either by heating to 220° C. in vacuo or in a current of air, or by passing ammonia over the mass heated to 180° C.

359,234. *Separating mixtures of gases—carbon monoxide.*

Naamlooze Vennootschap de Bataafsche Petroleum Maatschappij. 6th November, 1929.

Carbon monoxide and/or diolefines are recovered from gases or vapours by bringing them into contact with a neutral solution of a cuprous salt, such as cuprous chloride or formate containing a substance which prevents the formation of cupric salt, e.g. a reducing agent such as hydroxylamine hydrochloride. The absorbed compounds may be obtained by heating the liquid, e.g. to 40-80° C., or by applying reduced pressure, or both.

377,193. *Separating mixtures of gases.*

I.G. Farbenindustrie, A.G. 16th April, 1931.

The separation of gaseous hydrocarbons having a triple carbon linkage such as acetylene from gas mixtures, is effected by washing the mixtures with liquefied substances which under atmospheric pressure are gaseous at 15° C., and condensable at a temperature above 100° below 0° C., but other than substances chemically converting the unsaturated hydrocarbons during the washing operation, such as chlorine and substances themselves composed of unsaturated hydrocarbons. Suitable substances are those which may be used as cooling agents in refrigerating plants, i.e. liquid sulphur dioxide, ammonia, carbon dioxide, methyl chloride and ethyl chloride.

359,421. *Catalytic hydrogenation—hydrogen.*

I.G. Farbenindustrie, A.G. May, 1930.

To remove acetylene contained as an impurity in gases containing hydrogen, the gases are passed at 100-200° C. over a catalyst prepared from both chromium and nickel salts, oxides or hydroxides with or without other salts, or oxides or hydroxides. The acetylene is partly converted to ethane and partly polymerised.

The Production of Hydrogen from Hydrocarbons.

364,106. *Dehydrogenating hydrocarbons, carbon monoxide, hydrogen.*

I.G. Farbenindustrie, A.G. August, 1930.

In the conversion of mixtures of gaseous hydrocarbons into hydrocarbons poorer in hydrogen, and hydrogen, at elevated temperatures, the initial material is heated in stages at successively increased temperature so that the hydrocarbons which do not at first participate in the reaction are converted in the subsequent stage or stages, temperatures up to 1000° C. being employed in those stages in which mainly hydrocarbons having two or more carbon atms. are converted, while temperatures above 1000° C. are employed in the stages in which mainly methane is converted. It is preferable to desulphurise the gases before working up and the treatment may be carried out at high pressures 20-50 atms. or more.

An example of the proposals include (1) a gas mixture, obtained by the destructive distillation of coal, is mixed with an equal volume of steam, and passed at 700° C. over zinc oxide. Water is separated, then the unsaturated hydrocarbons are removed by cooling to − 50° C. Ethylene is washed out by means of bromine from the non-condensed gases which are then led at 900° C. through a producer filled with coke. Aromatic hydrocarbons, hydrogen and carbon black are obtained. (2) A gas mixture, obtained by the destructive hydrogenation of brown coal tar, is passed through four producers filled with coke at temperatures of 750-800-850-900° C. After each stage the unsaturated hydrocarbons are removed and the residual gas is led together with an excess of steam over a catalyst consisting of aluminium oxide and nickel, the methane being converted into hydrogen with partial formation of carbon monoxide and dioxide.

364,419. *Catalytic production of hydrogen.*

Standard I.G. Co. March, 1931.

In the catalytic production of hydrogen from hydrocarbon gases and steam the catalyst is periodically regenerated by the passage of steam alone. Preferably a number of reaction chambers are connected in parallel and each is regenerated in turn. The catalyst may be nickel and/or nickel oxide, with or without alumina, and the temperature of the catalytic reaction exceeds 1200° F. The invention is particularly applicable to the treatment of hydrocarbons containing heavy unsaturated constituents.

366,107. *Cracking hydrocarbons—hydrogen—carbon monoxide—catalytic apparatus.*

I.G. Farbenindustrie, A.G. September, 1930.

In thermal treatment of organic products, such as the cracking of oils, the conversion of methane and its homologues with steam or carbon dioxide into carbon monoxide and hydrogen, or in the reduction of phenol, cresol and the like with hydrogen, the deposition of carbon is avoided by providing the surfaces of ceramic apparatus which come into contact with the hot organic materials with a complete or partial covering of oxides of chromium, tungsten, vanadium or uranium. An example is as follows: An internally unglazed porcelain tube is soaked with a 50 per cent. aqueous chromic acid, and dried at 400° C., this being repeated three times. Methane is passed through this tube at 1075-1100° C., to produce benzene hydrocarbons and hydrogen.

380,164. *Separating mixtures of gases. Destructive hydrogenation.*

I.G. Farbenindustric, A.G. June, 1931.

In the separation of hydrocarbons from gases containing different proportions of hydrogen, the gas richer in hydrogen is first washed with a suitable solvent to lower the hydrocarbon content, preferably to the concentration of the gas poorer in hydrocarbons. The gases are then mixed and subjected to a further washing with a solvent for the hydrocarbons, if desired under different conditions.

The process is applicable to the gases obtained in the destructive hydrogenation of coals, tars, mineral oils, etc., so that the hydrogen obtained may be re-used, or to the removal of hydrocarbons from gases used in the synthesis of ammonia.

The process may be carried out in a single or separate washer, and in the latter case different pressures of the order of 200-280 atms. may be used. Suitable washing liquids include destructive hydrogenation products, e.g. those boiling between 180-220° C.

381,072. *Hydrogen catalysts.*

Naamlooze Vennootschap de Bataafsche Petroleum Maatschappij.
February, 1932.

In the production of hydrogen by the catalytic decomposition of gaseous hydrocarbons such as methane, ethane or ethylene, the catalysts employed consist of a mixture or compounds of the oxides of the iron group (iron, cobalt or nickel) with the acid forming oxides of the A sub-groups of the fourth, fifth and sixth groups of the periodic table, having a melting-point above 800° C.

Examples of catalysts are nickel vanadate, titanate or tungstate, cobalt uranate or vanadate, and iron vanadate or tungstate.

299,167. *Separating mixtures of gases.*

I.G. Farbenindustrie, A.G. September, 1927.

Pure hydrogen is recovered from mixtures by scrubbing at a temperature below 60° C., and preferably at high pressures with benzines that do not freeze at this temperature. In an example, a benzine of low boiling-point is atomised in a scrubber arranged on the counter flow principle, by means of a pressure slightly greater than that in the scrubber itself. Hydrogen containing about 8 per cent methane, together with other impurities, is introduced into the scrubber under a pressure of 50 atms. and at a temperature of 80° C. The recovered hydrogen is free from catalyst poisons, such as ether, carbon monoxide, hydrogen sulphide and carbon bisulphide.

341,462. *Hydrogen.*

Tyrer and Imperial Chemical Industries Ltd. October, 1929.

Hydrogen or gases containing hydrogen are obtained by the alternate supply of air and hydrocarbon gas with or without steam, to a bed of coke or refractory material, the blow gases being burnt with secondary air in an annular chamber surrounding the bed of coke or the like.

347,601. *Gas mixtures for ammonia synthesis.*

Tyrer and Imperial Chemical Industries Ltd. January, 1930.

A mixture of gases suitable for the synthesis of ammonia is prepared in a coke cooling plant by treating the hot coke simultaneously with water and air, and passing the gases without intermediate condensation of steam to an apparatus in which the carbon monoxide is converted to its equivalent of hydrogen by causing it to undergo a catalytic reaction with steam.

349,060. *Hydrogen.*

I.G. Farbenindustrie, A.G. November, 1929.

Hydrogen or a mixture thereof with other gases, such as carbon monoxide, is obtained by treating hydrocarbons or materials containing the same with air or oxygen in a chamber substantially free from carbonaceous matter to produce complete or substantially complete oxidation and the resulting gas mixture is then caused to act on heated carbonaceous matter, such as coal or coke. Combustion of the hydrocarbons is effected in a chamber separate and distinct from the first chamber and excess of oxygen may be used. The hot gases are conducted, together with additional water vapour, over hot coke and a mixture of hydrogen and carbon monoxide is formed, together with nitrogen when air is used for combustion. Catalytic conversion of the carbon monoxide to dioxide and absorption of the latter may be effected when desired, and the mixture used for the synthesis of ammonia.

366,369. *Catalytic production of hydrogen.*

Standard I.G. Co. April, 1931.

In the catalytic production of hydrogen, from hydrocarbons, gases and steam, the catalyst is periodically reactivated by the passage of a gas comprising oxygen free from hydrocarbons. The oxygen may be diluted with inert gases, such as nitrogen and carbon dioxide and with water vapour. A mixture of air and steam containing 5-30 per cent. of air is suitable. The invention is particularly suitable for the treatment of hydrocarbons containing unsaturated constituents such as natural or refinery gas.

366,494. *Catalytic apparatus—cracking oils—production of hydrogen.*

I.G. Farbenindustrie, A.G. September, 1930.

The conversion of methane into hydrocarbons of higher molecular weight is effected in apparatus constructed at least in part of chromium, molybdenum tungsten or alloys of these metals, with one another or of graphite. An example of the latter is given, and is as follows : If a gas containing 86·4 per cent. of methane is passed through a graphite tube enclosed in a quartz or chamotte tube externally heated by an electric furnace to 1000-1020° C., the exit gases contain 64·5 per cent. of methane, 26·8 per cent. hydrogen, and the condensate boils below 110° C.

376,358. *Catalytic production of hydrogen.*

I.G. Farbenindustrie, A.G. April, 1931.

Hydrogen is obtained by treating hydrocarbons having a higher molecular weight than methane with a gas capable of converting carbon into carbon monoxide such as steam, oxygen or carbon dioxide at a temperature between 400-1000° C., preferably 600-800° C., and more particularly 700-750° C., in the presence of a catalyst obtained by making an aqueous paste comprising at least one substance from the metals of the iron group, their oxides, hydroxides or carbonates and a hydraulic binding agent and allowing the paste to set. The catalyst may contain 20-90 per cent. of binding agents. Suitable raw materials for the source of hydrogen are the waste gases from destructive hydrogenation of coal, tars and mineral oils, etc. Details of suitable binding agents are given.

CHAPTER IV.

THE DESIGN OF PRESSURE VESSELS FOR SERVICE AT ORDINARY TEMPERATURE.

IT is not intended in this book to deal with riveted construction of pressure vessels, since this form of manufacture is only applicable to comparatively low pressures, and it is dealt with at considerable length in all textbooks on steam boiler construction. Unless otherwise stated, all pressure vessels described in this book are of the hollow forged or seamless type.

A full description of the technique of the manufacture of hollow forged high-pressure vessels is given in Chapter X., wherein will also be found particulars of welded construction of such vessels which, although not practised in Great Britain, is used extensively abroad, notably in the United States and Germany.

In Great Britain welded construction of high-pressure vessels working at temperatures appreciably higher than 100° C. has been discouraged by the Board of Trade and the various Insurance Companies. The reasons for this were recently discussed at considerable length in a paper by Schuster (*Proc. Inst. Mech. Eng.*, 1930, 319).

At the present time in Great Britain the only official regulation governing pressure vessels (from the point of view of welding of seams) is the Board of Trade rule that prohibits, with certain minor exceptions, the use of a welded joint for plates in tension on boilers. For steam pipes there is another rule that permits a seam to be welded only when it is hammered or rolled, and in which case a minimum safety factor of 13, plus a wastage allowance, is specified. In the case of high-pressure air bottles for Diesel engines the Board of Trade require that seamless solid-drawn construction must be adopted. For unfired pressure vessels rules for riveted and solid-drawn construction alone are given, so that it is apparent that the intention is to discourage welded construction.

An enquiry is held by the Board of Trade on explosions of many types of steam and other pressure vessels, and the Home Office, whose special function is the protection of employees, has power to order an enquiry into any accident occurring in a factory. Naturally, official regulations that have been framed play an important part in regard to the verdict given on an accident to a pressure vessel.

The various Factory Acts in Great Britain make it compulsory for owners of most types of steam boilers to have these examined by a competent authority at least once a year, and the responsibility for selection of the competent person rests with the owner or occupier. In practice, the majority of such vessels in this country are surveyed by one of the Boiler Insurance Companies who are prepared to insure such vessels as a result of an exhaustive first and subsequent annual inspection. These inspections are carried out by competent engineers, who in most instances have had considerable marine experience.

In these circumstances it is not surprising that welded construction has made but little progress in this country in so far as high-temperature high-pressure plant is concerned. Whilst, as one who for some years was a surveyor with a prominent Boiler Insurance Company, I have every sympathy with their viewpoint, I am of opinion that in the general interest of all concerned in this matter they should carry out a concerted, comprehensive investigation into the whole subject with a view to proving or disproving the many claims made for welded work. There is no doubt that failures of welded vessels in the early stages of development of this process have made the Insurance Companies very nervous about accepting such construction, but in view of the special methods of fabrication developed by such firms as Thyssen of Germany and Kellogg of New Jersey, U.S.A., it would appear desirable that the possibility of fabrication by these or similar methods in this country should not be excluded because of early failures by quite unsatisfactory technique.

Quite recently a British Standard Specification has been issued (No. 487—1933) which gives particulars of fusion welded air receivers for stationary purposes. It contains much useful information regarding permissible types of welding for unfired pressure vessels. It is to be noted, however, that this specification refers only to *unfired* pressure vessels for comparatively low pressures.

Having now explained the reason for seamless or hollow forged construction of high-pressure high-temperature vessels for service in this country, the following discussion refers to the design of such seamless vessels for service at or about room temperatures. From the point of view of stress calculations it is convenient to divide such vessels into three groups :—

(1) Vessels for service at pressures not higher than 150 atms., and in which the "thin cylinder" formulæ can be applied. (The upper limit may be raised if high tensile alloy steels are used, when the working stress permitted may be as high as 20 tons per sq. in., instead of 8 tons, as for low carbon steels.)

(2) **Vessels for service between 150 atms. and 3000 atms.,** in which Lamé's theory, based on the validity of Hooke's Law, can be applied.

(3) **Vessels for service at pressures over 3000 atms.,** in which cases the accepted formulæ for lower pressures cannot be applied, because, material at the inner surface of such cylindrical vessels is initially stressed beyond the true limit of proportionality of any suitable material; and, secondly, the work hardening effect or "autofrettage" often used in their construction raises the limit of proportionality of the inner skin without materially affecting the portions more remote. Naturally at the present time vessels for pressures much over 1000 atms. are of a purely experimental character, but since several investigators are now carrying out chemical experiments at pressures over 3000 atms., it is considered desirable to deal later with such vessels at some considerable length.

Let us now examine the three categories of pressure vessels, and illustrate each type by reference to actual designs which have stood the test of long exposure to the desired conditions.

In the first group, an excellent example is the ordinary commercial gas cylinder, such as is used for conveying or storing the "permanent" gases at standard pressures of 120 atms. In this country, such vessels are made to one of two British Standard Specifications. These are B.S.S. No. 400, dated 1931, for "Low Carbon Steel" cylinders, and B.S.S. No. 399, 1930, for "High Carbon Steel" cylinders for the storage and transport of permanent gases. By permanent is meant gases such as atmospheric air, oxygen, nitrogen, hydrogen, etc., which at the usual working temperature and pressure remain in a gaseous state in the cylinder.

Until the recent adoption of the above specifications, all cylinders for the permanent gases in this country were made and used on the basis of the recommendations of the Home Office Committee of 1895, and which were as follows :—

Cylinders of Compressed Gas (Oxygen, Hydrogen or Coal Gas).

(a) *Lap-welded Wrought Iron.*—Greatest working pressure, 120 atms., or 1800 lbs. per sq. in.

Stress due to working pressure not to exceed 6½ tons per sq. in.

Proof pressure in hydraulic test, after annealing, 224 atms., or 3360 lbs. per sq. in.

Permanent stretch in hydraulic test not to exceed 10 per cent. of the elastic stretch.

One cylinder in 50 to be subjected to a statical bending test and to stand crushing nearly flat between two rounded knife edges without cracking.

(*b*) *Lap-welded or Seamless Steel.*—Greatest working pressure, 120 atms., or 1800 lbs. per sq. in.

Stress due to working pressure not to exceed 7½ tons per sq. in. in lap-welded, or 8 tons per sq. in. in seamless cylinders.

Carbon in steel not to exceed 0·25 per cent., or iron to be less than 99 per cent.

Tenacity of steel not to be less than 26 or more than 33 tons per sq. in. Ultimate elongation not less than 1·2 ins. in 8 ins. Test bar to be cut from finished annealed cylinder.

Proof pressure in hydraulic test, after annealing, 224 atms., or 3360 lbs. per sq. in.

Permanent stretch shown by water jacket not to exceed 10 per cent. of elastic stretch.

One cylinder in 50 to be subjected to a statical bending test and to stand crushing nearly flat between rounded knife edges without cracking.

REGULATIONS APPLICABLE TO ALL CYLINDERS.

Cylinders to be marked with a rotation number, a manufacturer's or owner's mark, an annealing mark with date, a test mark with date. The marks to be permanent and easily visible.

Testing to be repeated at least every two years and annealing at least every four years.

A record to be kept of all tests.

Cylinders which fail in testing to be destroyed or rendered useless.

Hydrogen and coal-gas cylinders to have left-handed threads for attaching connections, and to be painted red.

The compressing apparatus to have two-pressure gauges and an automatic arrangement for preventing overcharging. The compressing apparatus for oxygen to be wholly distinct and unconnected with the compressing apparatus for hydrogen and coal gas.

Cylinders not to be refilled till they have been emptied.

If cylinders are sent out unpacked, the valve fittings should be protected by a steel cap.

A minimum weight to be fixed for each size of cylinder in accordance with its required thickness. Cylinders of less weight to be rejected.

CYLINDER FITTINGS.

No oil or similar lubricant to be used for cylinder valves, pressure gauges, regulators or other fittings.

Pressure gauges to have a check to prevent a sudden inrush of gas.

Pressure gauges for hydrogen and coal gas to have left-handed screws, and to be painted red.

In November, 1918, a Gas Cylinders Research Committee was formed by the Advisory Council of the Committee of the Privy Council for Scientific and Industrial Research, with the following terms of reference :—

> "To re-examine the whole question of cylinders for the storage and transport of compressed gases other than acetylene, including the standardisation of the fittings of gas cylinders and to undertake the necessary experimental investigations."

A considerable amount of research work was carried out in this connection, and the recommendations of the Committee are set forth in four reports, published by H.M. Stationery Office. These are as follows :—

(1) The First Report of the Gas Cylinders Research Committee, 1921.

This report deals with the ordinary commercial gas cylinders for 120 atms. pressure for the storage and transport of the permanent gases. Prior to the adoption of the recommendations of this report, nearly all gas cylinders in this country were made of low carbon steel in which the permissible stress was 7½-8 tons per sq. in. With the object of saving weight (which is considerable compared with the weight of gas contained therein) the Committee recommended the alternative of cylinders made from a high carbon steel in which case the permissible stress could be raised to 10 tons per sq. in. Hence, for the same capacity these high carbon steel cylinders would weigh approximately 20 per cent. less than low carbon steel cylinders. This means of course that considerably less physical effort is required to handle the cylinders, and transport costs are correspondingly reduced.

The following is a brief résumé of the principal recommendations of the majority report of this Committee :—

(1) The cylinders should be solid drawn.

(2) The steel used in the manufacture of the cylinders shall have the following composition :—

Carbon	0·43 to 0·48 per cent.
Manganese	0·50 to 0·90 ,,
Silicon	Not to exceed 0·30 per cent.
Sulphur	,, ,, 0·045 ,,
Phosphorus	,, ,, 0·045 ,,
Iron	The remainder.

(3) (*a*) The steel used in the manufacture of the cylinders shall be made by the acid or basic open-hearth process.

(*b*) The steel ingot should be commercially free from unsoundness and segregations, and in the cropping of the ingot all piped and segregated material should be removed.

(*c*) Blooms and billets for the manufacture of cylinders should be supplied with a guarantee from the steelmaker that the ingots from which they have been produced have been made by an approved process.

(*d*) Facilities for the inspection of steel at the steelmakers' works should, if so desired, be afforded to the representative of the cylinder manufacturer, and facilities should be afforded by a system of marking and registration of billets to enable the material from which the cylinders are made to be identified.

(4) All cylinders shall, after manufacture, be raised to a temperature of not less than 820° C., and not exceeding 850° C., remaining within the furnace for a time sufficient to ensure that all parts of the cylinder have reached that temperature, and no longer than that time. Before the temperature falls appreciably, they shall be removed and allowed to cool in still air in such a position that they are not subjected to draughts.

(5) Mechanical tests shall be made on the material of one finished cylinder in every batch, or when the number in any batch exceeds 100, on the material of at least one finished cylinder in every 100.

The tests shall be made on a strip, cut longitudinally from the finished cylinder. The results shall conform to the following conditions :—

(*a*) The yield stress shall not be less than 20 tons per sq. in.

(*b*) The ultimate stress shall not be less than 40 tons per sq. in.

(*c*) The elongation shall not be less than 14 per cent. on a 6-in. gauge length (or on a corresponding length in cases where a test piece geometrically similar to the standard specimens has to be used).

(6) Impact tests should be made on the material of cylinders which are not less than 6 ins. in diameter. The mean energy required for the fracture of three test pieces should not be less than 3 ft.-lbs. for the transverse test, and 5 ft.-lbs. for the longitudinal tests.

(7) Before the necking operation, each cylinder should be examined for maximum and minimum thickness, and for external and internal surface defects.

(8) The maximum working pressure of the cylinders should be 120 atms.

(9) The stress due to the working pressure should not exceed 10 tons per sq. in.

(10) The hydraulic test pressure should be $1\frac{2}{3}$ times the working pressure.

(11) The permanent stretch shown by the "water jacket" hydraulic test should not exceed 10 per cent. of the elastic stretch.

(12) Cylinders should be periodically examined to determine the amount of corrosion.

(13) Each cylinder should undergo the hydraulic test specified to 3000 lbs. per sq. in. at least once in two years.

(14) All cylinders should be marked with
- (*a*) Manufacturer's and owner's mark and rotation number.
- (*b*) Last date of hydraulic test.
- (*c*) Last date of heat treatment. (In this connection, see the recommendations contained in the second report of the Committee.)
- (*d*) A mark indicating the specification to which the cylinder has been made.

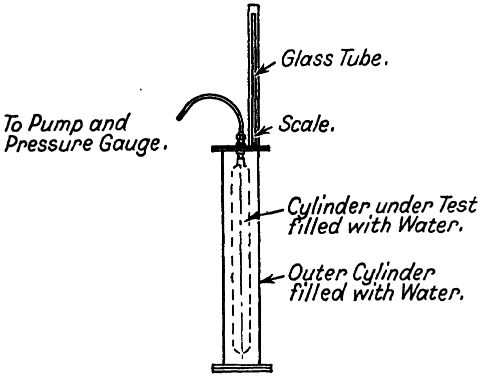

Glass Tube.
To Pump and Pressure Gauge.
Scale.
Cylinder under Test filled with Water.
Outer Cylinder filled with Water.

FIG. 81.—Hydraulic test of gas cylinder by water jacket method.

(15) In connection with the working stress, the Committee recommend this to be calculated from the thin cylinder formula

$$f = \frac{pd}{2t},$$

where f = maximum working stress, tons per sq. in.
p = internal pressure, tons per sq. in.
d = mean diameter of cylinder in inches.
t = wall thickness in inches.

This will correspond to a factor of safety as commonly understood of about 4.

(16) Regarding the hydraulic test, the Committee recommend the test be carried out by the water jacket method, which is illustrated in Fig. 81. The cylinder under test is filled with water and having

a gauge glass projecting from its upper cover provided with a scale on which the level of the water may be read. The rise of water in the gauge glass during the test is a measure of the elastic and permanent extension of the cylinder, and the difference in the readings before and after the proof pressure is applied will indicate the permanent extension.

In the 1895 Report it was stated that a permanent extension of not exceeding 10 per cent. of the elastic extension may probably be safely disregarded, and in the opinion of the 1921 Committee this may safely be allowed.

(17) The Committee also recommend that one finished cylinder in every batch, the minimum being one in every 100, should be subjected to a flattening test of the following description : the middle part of an empty cylinder should be placed between two compression blocks having flat faces $2\frac{3}{4}$ ins. wide with corners rounded to $\frac{1}{4}$ in. radius, and pressure applied until cracks appear at the folded surface of the cylinder between the compression blocks. The test shall be deemed unsatisfactory if the distance between the faces of the blocks in contact with the cylinder when cracks appear is more than eight times the wall thickness of the cylinder.

As stated in the first paragraph of this summary, these recommendations were made by the Majority Report of the Committee. Mr. J. H. B. Jenkins compiled a Minority Report because he considered that to adopt the lighter and harder " high carbon " steel cylinder was, in his opinion, to move in the direction of danger, and he gave a considered report with reasons for his opinion.

Briefly, his objection to the higher carbon steel cylinder was that he considered this type of steel inferior in toughness (or resistance to impact), and that there is a greater variability in this property than in the case of the 0·25 per cent. or " low carbon " steel cylinder. Hence he questioned the advisability of applying it to gas cylinders where toughness or resistance to impact is so important.

As a result of the reports of this Committee, commercial gas cylinders in this country are now made to one of two British Standard Specifications in so far as the storage and transport of the permanent gases is concerned.

These are British Standard Specification No. 400 for " Low Carbon " steel gas cylinders, and B.S.S. No. 399 for " High Carbon " steel gas cylinders for permanent gases. The former varies from the latter in respect of the carbon content of the steel (low carbon 0·20-0·25 per cent. C., high carbon 0·43-0·48 per cent. C.), and the permissible working stress (low carbon 17,920 lbs. per sq. in., high carbon 22,400 lbs. per sq. in.), and the yield point and ultimate tensile test figures, etc., are arranged correspondingly.

(2) The Second Report of the Gas Cylinders Research Committee, 1926.

This deals with the former practice of periodical heat treatment of cylinders. The report concludes with :—

> "The Committee agree that the results indicate that the periodical heat treatment of carbon steel gas cylinders which have not been obviously damaged serves no useful purpose, and they recommend that the practice be discontinued."

(3) The Third Report of the Gas Cylinders Research Committee, 1929.

This report deals with the subject of special alloy steel light cylinders suitable for carrying on aircraft, for mine rescue and medical work.

The recommendations of the Committee were as follows :—

SUMMARY OF RECOMMENDATIONS REGARDING LIGHT CYLINDERS OF NICKEL CHROMIUM MOLYBDENUM STEEL FOR THE STORAGE AND TRANSPORT OF "PERMANENT" GASES.

In special cases where it is highly important to have very light small cylinders, we recommend the use of nickel-chromium-molybdenum steel cylinders for the storage and transport of "permanent" gases, subject to the fulfilment of the following conditions :—

1. Chemical Composition.

The steel used should have the following composition :—

Nickel	2·5 per cent.
Chromium	0·6 ,,
Molybdenum	0·6 ,,
Manganese	0·6 ,,
Carbon	0·3 ,,
Silicon	0·15 ,,
Sulphur	0·04 maximum.
Phosphorus	0·03 ,,

2. Tests with which the Material and the Finished Cylinders should conform.

A. *Material.*

Material from which specimens can be cut should be supplied by the manufacturer as follows :—

Specimens 1 in. sq. and 8 in. long cut from one of the forged billets from which the cylinders are made, and heat-treated with the finished cylinders ; at least one such specimen should be taken from each cast.

The mechanical properties of this material should be :—

Ultimate tensile strength 55 to 65 tons per sq. in.

Yield stress, not less than 45 tons per sq. in.

Elongation, not less than 18 per cent. on 2-in. gauge length, with a standard specimen 0·564 in. diameter.

B. *Finished Cylinders.*

After the final heat-treatment of the finished cylinders by the manufacturers, they should pass the following tests :—

(i) Each completed cylinder should be subjected to a hydraulic proof pressure of 2700 lb. per sq. in. The ratio of the permanent set to the total stretch under the proof pressure (to be determined, preferably by the "water jacket" method which was described in the First Report) should not exceed 0·1.

(ii) Each cylinder that passes the test specified in 2 B (i) above should be subjected to an internal hydraulic pressure of 2550 lb. per sq. in. in the open, and should show no signs of leak.

(It is understood that a method determining the ratio of the permanent set to the total stretch (Clause 2 B (i), in which the cylinder is not enclosed in a water jacket but left exposed, is in considerable use in the compressed gas industry. This method can only be relied upon to give accurate results when somewhat elaborate precautions are taken to exclude air from the apparatus, and when corrections are made for the compressibility of water. For these reasons the "water jacket" method is, in our opinion, to be preferred. The relative merits of the two methods will be discussed in somewhat greater detail in a forthcoming report on cylinders for "liquefiable" gases. If, however, this other method, with the precautions indicated, should be used, it will be obvious that as the cylinder is left exposed, the observation indicated in Clause 2 B (ii) can be made at the same time, and a separate test for this purpose will be unnecessary.)

(iii) One cylinder in every batch, with a minimum of one in every 25 should be filled with air at a pressure of 1800 lb. per sq. in., and be perforated by 0·303 in. armour-piercing bullet (Ammunition Mark VII. P). In the event of any one of the cylinders bursting (either with or without fragmentation) further cylinders in the proportion of two for every previous one should be similarly tested. Should any of these burst, the whole batch should be rejected.

A record should be kept of all tests made at the cylinder-maker's works, and copies forwarded to the purchasers of the cylinders.

3. Design and Capacity.

The cylinders should be seamless and weldless and of a capacity of 20 cu. ft. of free gas ; the closed end of each cylinder should be hemispherical in shape and the neck end should be either hemispherical or conical. The outside and inside surfaces should be finished smooth.

4. Design of Neck.

If the cylinder neck is closed down to the same extent as those described in this report (i.e. tapped with a $\frac{3}{8}$-in. gas thread), a steel collar should be shrunk over the neck. The neck should project beyond the end of the collar by about $\frac{1}{32}$ in. and the collar should fit closely into the cylinder shoulder without leaving any space in which dirt and moisture may collect.

5. Working Pressure.

The internal working pressure should not be greater than 1800 lbs. per sq. in.

6. Working Stress.

The maximum working stress should not exceed 25 tons per sq. in. when calculated from the formula

$$f = \frac{p(D - t)}{2t},$$

where f = maximum working stress, tons per sq. in.
p = maximum internal working pressure, tons per sq. in.
D = external diameter in inches.
t = thickness of wall in inches.

7. Wall Thickness.

A tolerance on wall thickness of + 20 per cent. may be allowed; this is intended to cover a certain amount of eccentricity of bore, and does not permit of a general tolerance of more than + 10 per cent. on wall thickness.

The thickness of the cylinder wall for cylinders of 4 in. outside diameter should not be less than 0·080 in.

8. Heat-Treatment.

The details of the heat-treatment to which the cylinders are to be subjected should be left to the discretion of the manufacturer, and should be such as to enable the cylinders and material to pass the tests detailed in Clauses 2 A and 2 B.

9. Cleaning.

Particles of scale, oil, grit, filings or other matter, which may have collected inside cylinders in course of manufacture, heat-treatment or testing, should be carefully removed.

10. Periodical Examination.

Each cylinder should be subjected to the hydraulic test specified in Clause 2 B (i) at least once in every two years. Prior to each periodical test the cylinder should be thoroughly cleaned and examined externally and, as far as practicable, internally, for surface defects, corrosion or foreign matter. Except where the opening of the neck is not sufficiently large, a small electric lamp inserted into the cylinder is useful for the purpose of internal examination. Where internal rust or foreign matter is observed, the cylinder should be heated to a temperature not exceeding 300° C., and again cleaned and examined. After passing the hydraulic test, the cylinder should be thoroughly dried.

Apart from the above, no heat-treatment should be given to these cylinders after they have been delivered by the manufacturer. A cylinder should not be retained in service if it is suspected that it has been overstrained or has been damaged in any way.

11. Fittings.

(i) Cylinders which are to contain inflammable gases should be fitted with valves having left-hand outlet threads for pipe connection.

(ii) No oil or similar lubricant should be used on valves or other fittings.

12. Marking.

Every cylinder should be marked with—

(i) Manufacturer's and owner's mark and rotation number.
(ii) Date of last hydraulic test.
(iii) Chemical symbols (to be stamped on the valve) to indicate the gas for which the cylinder is used.

No cylinder should be marked on any part of the body; all marks should be stamped on the neck or neck collar, except as specified in (iii) above, and should be permanent and easily visible.

13. Painting.

Each cylinder should be painted, according to the gas for which it is used, as specified in the scheme recommended by the British Engineering Standards Association.

14. Packing for Transit Purposes.

During transit cylinders should be placed in cases or crates to protect the cylinder and valve. The cases or crates may be made to contain more than one cylinder, provided each cylinder is placed in a separate compartment.

(4) The Fourth Report of the Gas Cylinders Research Committee, 1929.

This report is concerned with cylinders for the conveyance of the liquefiable gases, that is those gases which have a relatively high critical temperature, and which are generally reduced to the liquid condition by the pressures used in charging them into the cylinders.

The subject of containers for the liquefiable gases was dealt with by the Home Office Committee of 1895, but only to a limited extent, and recommendations were given for but two such gases, namely, carbon dioxide and ammonia.

The gases investigated by the committee were :—

1. Sulphur dioxide.
2. Ammonia.
3. Chlorine.
4. Methyl chloride.
5. Ethyl chloride.
6. Hydrocyanic acid.
7. Phosgene.
8. Carbon dioxide.
9. Nitrous oxide.
10. Ethylene.

The generally accepted values of the critical temperature and pressure of purified samples of various gases have been published by the Bureau of Standards (Bureau of Standards Scientific Paper No. 541, 1926).

The following table gives these particulars :—

Gas.	Symbol.	Boiling-Point. °C.	Critical Temperature. °C.	Critical Pressure. Atms.
1. Sulphur dioxide	SO_2	− 10·8	157·2	77·7
2. Ammonia	NH_3	− 33·5	132·4	111·5
3. Chlorine	Cl_2	− 33·6	144	76·1
4. Methyl chloride	CH_3Cl	− 24·1	143·1	65·8
5. Ethyl "	C_2H_5Cl	12·5	187·2	52
6. Hydrocyanic acid	HCN	26·1	183·5	52·3
7. Phosgene	$COCl_2$	8·2 at 756 mm.	182	56
8. Carbon dioxide	CO_2	− 78·2	31·1	73
9. Nitrous oxide	N_2O	− 89·8	36·5	71·7
10. Ethylene	C_2H_4	− 102·7	9·7	50·9

The principal recommendations of the Fourth Report for ordinary commercial cylinders for the storage and transport of liquefiable gases are briefly as follows :—

(1) The cylinders should be made of carbon steel having the following approximate composition :—

Carbon	0·20 to 0·25 per cent.
Manganese	0·45 to 0·75 "
Silicon	Not to exceed 0·2 per cent.
Sulphur	" " 0·045 "
Phosphorus	" " 0·045 "
Iron	The remainder.

(No alloy steel should be used for this purpose.)

(2) General conditions recommended for the supply of the steel are as for the "high carbon" steel cylinders in the First Report (see page 150). The cylinders should be made of seamless steel tube.

(3) The thickness of the cylinder wall should be not less than the value of t in inches, as given by the following formulæ :—

(*a*) When the working pressure is 1500 lbs. per sq. in. or over,

$$t = \frac{pD}{2f + p}. \qquad (2)$$

(*b*) When the working pressure is 500 lbs. per sq. in. or less,

$$t = \frac{pD}{4f}\left(1 + \sqrt{1 + \frac{633f}{p^2D}}\right). \qquad (3)$$

(*c*) When the working pressure is between 500 lbs. per sq. in. and 1500 lbs. per sq. in.,

$$t = t_3 + (t_2 - t_3)\left(\frac{p}{1000} - 0{\cdot}5\right), \qquad (4)$$

where p = maximum internal working gauge pressure ; lb. per sq. in.

D = external diameter in inches.

f = 17,920 lbs. per sq. in.

t_2 = value of t in formula (2), taking p as 1500 lbs. per sq. in., and the required value for D.

t_3 = value of t in formula (3), taking p as 500 lbs. per sq. in., and the required value of D.

(4) Before the necking operations, each cylinder should be examined for maximum and minimum thickness, and for internal and external surface defects.

(5) Cylinders after manufacture should be raised to a temperature not less than 860° C., and not exceeding 890° C., remaining in the furnace only for a time sufficient to ensure that all the parts of the cylinder are at the same temperature.

Before the temperature falls appreciably they should be removed and allowed to cool in still air, free from draughts.

(6) Each cylinder, when not in use, should have its valve completely protected. An exception may be made in the case of the small cylinders not exceeding 10 lbs. of water capacity used for nitrous oxide.

(7) The water capacity of each individual cylinder should be carefully ascertained, and by using the appropriate filling ratio, the true gas capacity determined. The true gas capacity (in lbs.) added to the tare weight of the cylinder will give the gross weight required in Clause (8) (*f*) below.

(8) Every cylinder should be marked with :—

(*a*) Manufacturer's and owner's marks and rotation number.
(*b*) Date of last hydraulic test.
(*c*) A mark indicating the specification to which it has been made.
(*d*) Chemical symbols (to be stamped on the valve) to indicate the gas for which the cylinder is to be used.
(*e*) The internal pressure required for the hydraulic test.
(*f*) The tare and gross weights.

All marks should be stamped on the neck of the cylinder except marks (*d*), which should be on the valve, and the manufacturer's mark which may be on the base.

(9) Tensile tests should be made on the material of one finished cylinder in every batch, or in cases where the number in any batch exceeds 100, on the material of at least one finished cylinder in every 100.

The test should be made on a bar cut longitudinally, and should conform to the following :—

(*a*) Yield stress not less than 17 tons per sq. in.
(*b*) Ultimate stress not less than 28 tons per sq. in., nor more than 33 tons per sq. in.
(*c*) The elongation should be not less than 15 per cent. on following gauge lengths :—

Specimen Thickness.	*Gauge Length.*
Over 0·40 in.	8 ins.
0·20 to 0·40 in.	6 "
Less than 0·20 in.	4 "

(10) Another finished cylinder in every batch (or the same cylinder if the length permits a parallel portion four diameters long for the flattening test as well as tensile, etc., specimens) should be subjected to the same flattening test as given for the "high carbon" steel cylinders, except that the distance between the faces of the blocks when cracks appear should not be more than *four* times the wall thickness of the cylinder.

(11) Each completed cylinder when ready to be put into service should be subjected to an hydraulic stretch test, preferably by the water jacket method described in the case of "high carbon" steel cylinders. The test pressure should be found from the formula

$$p = \frac{2ft}{D - t},$$

where D = outside diameter of cylinder, f = hydraulic test pressure *stress* (not to exceed 33,600 lbs. per sq. in.), p = hydraulic test *pressure*, and t = thickness of cylinder walls.

(12) Each cylinder should be painted according to the gas for which it is to be used.

(13) Each cylinder should be hydraulically tested as specified at intervals of not more than two years.

(14) The specified filling ratio (weight of gas permitted per lb. of water capacity) should not be exceeded, and the accuracy of this should be determined by weighing.

(15) A notice should be attached to each charged cylinder to indicate that it should be kept cool.

These recommendations have been incorporated into British Standard Specification No. 401 (1931), and full particulars of filling ratios, test pressures, etc., are given therein.

All commercial gas cylinders of whatever type should be painted the distinctive colours recommended in British Standard Specification No. 349 (1931). For example, the underlying principle is that yellow should represent toxic or poisonous gases, and red or maroon inflammable gases.

British Standard Specification No. 341 (1931) gives particulars of valve fittings for compressed gas cylinders. In general, inflammable gases (hydrogen, methane, etc.), have *left-hand* screw connections, and gases such as air oxygen, nitrogen, *right-hand* fittings. The materials from which valves should be made are also given in this specification.

Cylinders and cylinder fittings should be carefully handled, and kept free from oil and grease. Records of any privately-owned gas cylinders should be carefully kept, and any occurrence of note should be duly entered in this log book.

Vessels Designed on "Thin Cylinder" Theory.

It is to be noted that the shells of all the gas cylinders described are designed on the basis of the "thin cylinder" theory, which is briefly as follows :—

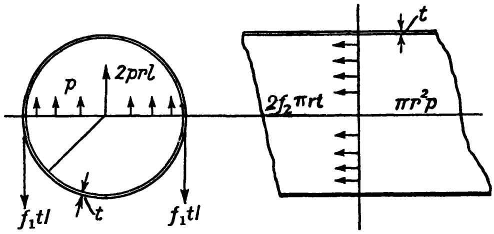


FIG. 82.—" Thin cylinder " theory of pressure vessel design.

If a thin circular cylinder is subjected to internal fluid pressure, a tensile stress arises in the walls of the material, and this is usually described as the " hoop stress." When the thickness of the cylinder walls is small compared with the internal diameter of the cylinder, it is assumed that the hoop stress is uniformly distributed throughout the cross-section of the material.

Referring to Fig. 82, let r be the internal radius, and t the thickness of a thin cylinder subjected to an internal pressure of p, causing a hoop tension f_1 in the walls of the cylinder. Considering the equilibrium of the half cylinder of length l,

$$2f_1l \, . \, t = 2p \, . \, r \, . \, l,$$

whence $$f_1 = \frac{pr}{t} \text{ or } \frac{pd}{2t},$$

where d = internal diameter of the cylinder.

If the cylinder be closed at the ends the shell will be subjected to a longitudinal tension as well as a hoop tension. So that if f_2 = longitudinal tension,

$$f_2,\ 2\pi rt = p\pi r^2,$$

whence $$f_2 = \frac{pr}{2t} \text{ or } \frac{pd}{4t},$$

whence it will be seen that the intensity of longitudinal stress is just half the circumferential or hoop stress.

In addition to the two principal stresses, f_1 and f_2, there is a third principal stress which is a radial pressure and varies from a maximum of p at the inner surface of the shell to zero at the outer surface; this stress is quite small in the cases where the thin cylinder theory is applicable, and hence is neglected.

The following is an example of a cylinder designed on the basis of the "thin cylinder" principle.

At the Chemical Research Laboratory, Teddington, there are two large high-pressure gas bottles, each of 3 cu. ft. water capacity, and made from heat-treated nickel chrome molybdenum steel. The bottles are used for pressures not exceeding 250 atms. at ordinary temperature, and are 6 ft. 6 ins. long, 9½ ins. internal diameter, and with ½-in. walls.

It is required to find the hoop stress in the walls of the shell. Note 250 atms. = 1·67 tons per sq. in.

$$\begin{aligned} f_1 &= \frac{pd}{2t} \\ &= \frac{1{\cdot}67 \times 9{\cdot}5}{2 \times 0{\cdot}5} \\ &= 16 \text{ tons per sq. in.} \end{aligned}$$

The steel from which the bottles were made was of similar chemical analysis and heat-treated to give mechanical properties as detailed for the 550 atms. gas bottle described in the next section.

If these bottles had been supplied in low carbon mild steel, to withstand the pressure the walls would of necessity have to be at least twice as thick, in which case the "thin cylinder" formula would not be applicable. In such circumstances it is necessary to apply the thick cylinder formulæ, and these will now be discussed.

Vessels for Service Between 150-3000 atms.

Thick Cylinders subjected to Fluid Pressure.

The following theory is due to Lamé :—

Let R_2 and R_1 respectively (Fig. 83) be the internal and external radii, and let p_2 and p_1 be the internal and external pressure intensities. Let p_x and p_y be the intensities of radial compression stress and circumferential tension respectively at any variable radius x, the third principal stress being parallel to the axis of the cylinder. Then considering the equilibrium of half of any very thin cylindrical element of radius x, thickness δx, and length l, the outward pressure on the curved surface, that is the outward resultant of the pressure on inside and outside, must be equal to the total hoop tension across a diametral plane or

$$(p_x \times 2xl) - (p_x + \delta p_x)2(x + \delta x)l = 2p_y l\delta x,$$

whence,
$$-p_x \,.\, \delta x - x\delta p_x - \delta x\delta p_x = p_y \,.\, \delta x,$$

and when δx is reduced indefinitely,

$$p_y = -p_x - x\frac{dp_x}{dx} = -\frac{d(p_x x)}{dx}. \qquad . \quad . \quad (1)$$

Another relation between p_x and p_y depends upon an assumption as to longitudinal strain. It is assumed that plane transverse sections remain plane under the pressure, an assumption which must be nearly true at considerable distances from the ends. This means that the longitudinal strain at any point in a cross-section is independent of x, and therefore constant.

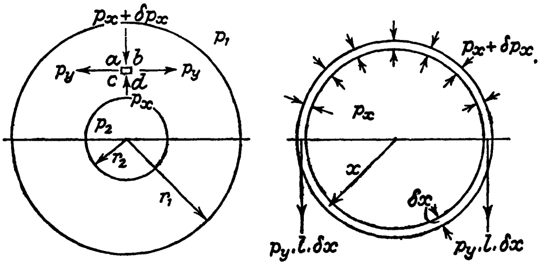


FIG. 83.

Hence
$$e = \frac{1}{E}\left(f_1 - \frac{p_y - p_x}{m}\right).$$

Since e, E and f_1 and m are constant, $p_y - p_x$ must be a constant.

Taking
$$p_y - p_x = 2a. \qquad . \quad . \quad . \quad . \quad (2)$$

Substituting for p_y its value from the first equation, we get

$$-2p_x - x\frac{dp_x}{dx} = 2a.$$

Whence
$$p_x = \frac{b}{x^2} - a, \qquad . \quad . \quad . \quad . \quad (3)$$

where a and b are constants to be determined from known internal and external radial pressures and radius.

Also we can get

$$p_y = \frac{b}{x^2} + a, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

When the external pressure is zero, from these equations we get

$$p_x = p_2 \frac{R_2^2}{R_1^2 - R_2^2}\left(\frac{R_1^2}{x^2} - 1\right), \quad . \quad . \quad . \quad (5)$$

$$p_y = p_2 \frac{R_2^2}{R_1^2 - R_2^2}\left(\frac{R_1^2}{x^2} + 1\right), \quad . \quad . \quad . \quad (6)$$

whence we find that the greatest intensity of hoop stress in a cylinder is at the inner skin of the metal next to the bore (and where $x = R_2$), and is

$$p_{y2} = p_2 \frac{R_1^2 + R_2^2}{R_1^2 - R_2^2}. \qquad (7)$$

The greatest intensity of radial stress (p_x) is also at the inner skin next to the bore of a vessel, and is there numerically equal to the internal pressure p_2.

Some very interesting experiments in connection with the failure of thick cylinders when subjected to high internal pressure were carried out by Cook and Robertson (*Engineering*, 1911, **92**, 786). They were able to reach pressures as high as 15 tons per sq. in., and the following table gives particulars of the results obtained by bursting a mild steel cylinder of about 2 ins. outside diameter and with the stated ratio of external to internal diameter :—

TABLE 1.

Ratio External to Internal Diameter (K).	Ultimate Strength of Material. Lbs./sq. in.	Maximum Pressure (p). Lbs./sq. in.	Maximum Pressure Calculated from Formula $p = f\frac{K^2 - 1}{K^2 + 1}$.
1·35	54,400	16,900	15,800
1·53	54,400	23,200	21,900
1·58	54,400	24,850	23,400
1·67	58,800	27,200	27,700
1·67	58,800	27,350	27,700
1·71	58,800	30,200	28,700
1·77	54,400	30,850	28,000
1·79	54,400	30,500	28,600
1·79	54,400	32,300	28,600

From which, although Lamé's theory for the distribution of stress does not hold when the material is stressed beyond the elastic limit, it so happens that the values of the maximum pressure agree fairly closely, as will be seen from Table 1, with the values which would be obtained by calculation from Lamé's formula

$$p = f_{\text{ult}}\frac{K^2 - 1}{K^2 + 1}, \quad . \quad . \quad . \quad . \quad (8)$$

where f_{ult} = ultimate strength of material,

K = initial ratio $\frac{\text{external}}{\text{internal}}$ diameter,

p = maximum pressure.

Up to the yield point the authors found that the following equation held true :—

$$p = 0{\cdot}6f\frac{K^2 - 1}{K^2}, \quad . \quad . \quad . \quad . \quad (9)$$

where f is a hoop tensile stress not higher than the yield point.

The above results are, of course, only applicable to mild and other ductile steels, but there is no doubt that if suitable alloy steels are used for high-pressure work, and these are heat-treated to give good ductility, the data obtained by Cook and Robertson is quite applicable.

It is not permissible, of course, to apply these data to cylinders whose ratio external to internal diameter is considerably larger than those used by Cook and Robertson. The formula

$$p = f_{\text{ult}}\frac{K^2 - 1}{K^2 + 1}$$

means that if K is very great the expression becomes $p = f_{\text{ult}}$. This implies that an infinitely thick wall will not prevent a cylinder from failing if the applied internal fluid pressure is numerically greater than the ultimate strength of the material. This point will be enlarged later when the design of cylinders for pressures over 3000 atms. is discussed.

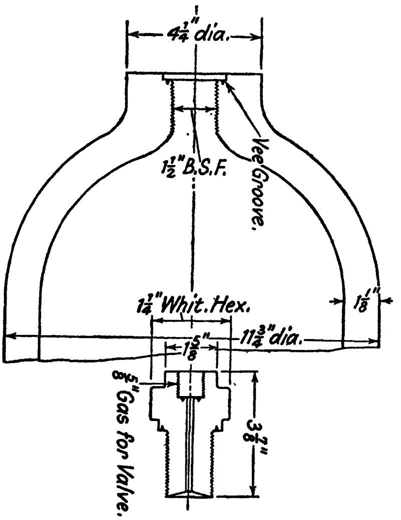


FIG. 84.—Neck of 550 atm. gas bottle

To resume the consideration of vessels for service between 200-3000 atms., the formulæ given by Cook and Robertson are quite reliable, and undoubtedly the best basis upon which to design plant (made from suitable alloy steel) within these pressure limits.

One or two examples of actual vessels in the design of which the foregoing reasoning has been applied will now be discussed. It is, perhaps, as well to repeat that in this chapter attention is confined to vessels working at ordinary temperature.

Firstly, a gas bottle in service at the Chemical Research Laboratory is shown in Fig. 84. It is used for the storage of gas at pressures not exceeding 550 atms. The internal diameter is $9\frac{1}{2}$ ins., and the outside diameter $11\frac{3}{4}$ ins., so that the ratio $K = \dfrac{11{\cdot}75}{9{\cdot}5} = 1{\cdot}24$, and $K^2 = 1{\cdot}54$. The gas pressure, $p = 550$ atms. $= 3{\cdot}7$ tons per sq. in. Since it is required to find the hoop stress in the material, and this stress is below the yield point, the equation (9) is used and substituting values given.

$$p = 0{\cdot}6f\frac{K^2 - 1}{K^2},$$

$$3{\cdot}7 = 0{\cdot}6f\frac{1{\cdot}54 - 1}{1{\cdot}54},$$

whence $f = 17{\cdot}6$ tons per sq. in.

The bottle was made from heat-treated V. 30 Vibrac steel of the following chemical composition, and tests gave the following mechanical properties :—

C	Si	P	S	Mn	Ni	Cr	Mo	Fe
0·4	0·24	0·031	0·029	0·57	2·51	0·68	0·5	Remainder

Yield Point.	*Ult. Tensile.*	*Elongation.*	*Reduction of Area.*
48·0 tons per sq. in.	58·5 tons per sq. in.	23·0 per cent.	62 per cent.

It will be seen that the design offers a good margin for safety.

Solid-drawn copper tubes $\frac{3}{8}$-in. outside diameter × $\frac{3}{16}$-in. bore are frequently used in experimental work for the conveyance of fluids or gas at pressures as high as 300 atms. Here the ratio $K = 2$ and $K^2 = 4$. Taking 300 atms. as 2 tons per sq. in. and substituting in the equation

$$p = 0{\cdot}6f\frac{K^2 - 1}{K^2},$$

we get $$2 = 0{\cdot}6f \times \frac{4 - 1}{4},$$

whence $$f = 4{\cdot}4 \text{ tons per sq. in.}$$

Alloy steel drawn tubing is used for pressures as high as 1000 atms., with outside diameter of $\frac{9}{16}$ in. and a bore of $\frac{3}{16}$ in. Taking 1000 atms. as 6·7 tons per sq. in., and $K = 3$ and $K^2 = 9$, we get

$$p = 0{\cdot}6f\frac{K^2 - 1}{K^2},$$

$$f = \frac{6{\cdot}7 \times 9}{8 \times 0{\cdot}6}$$

$$= 12{\cdot}5 \text{ tons per sq. in.}$$

Vessels for Service at Internal Pressures over 3000 atms.

As discussed earlier in this chapter, there is no theoretical basis upon which to design vessels for service at pressures much in excess of 3000 atms. Such vessels are naturally of an experimental character, and are comparatively small in dimensions, but several organisations are beginning chemical research under these severe conditions, and consequently the subject is becoming important.

At pressures in excess of 3000 atms., the internal fluid pressure is as high, if not higher than the figure for the true elastic limit of even the strongest alloy steels, and hence the material does not behave as an elastic body. In these circumstances it is impossible to determine the stress distribution throughout the vessel by theoretical reasoning, and the designer must base his scantlings upon experimental results. As already mentioned, Cook and Robertson have obtained valuable data, which are collected in Table 1. They found that the bursting pressure of mild steel cylinders was represented by the equation $p = f_{\text{ult}}\frac{K^2 - 1}{K^2 + 1}$, which means that the cylinder will burst when the internal fluid pressure is equal numerically to the ultimate tensile strength of the material, no matter how thick the vessel wall. It must be noted that this formula is a purely empirical one, and hence is only applicable to the experimental conditions from which it was derived; that is a material such as mild steel with a maximum ratio of $K = 1{\cdot}79$.

Using alloy steels, and considerably thicker cylinders, workers such as Bridgman, Michels, Poulter and Basset have found that simple cylinders under such conditions will withstand internal fluid pressures far higher than the ultimate tensile strength of the material from which they are made. Bridgman has carried out the most instructive series of tests in this connection, and he found that such cylinders when stressed to the limit fail by rupture of the external surface. This result is not so surprising as at first sight might appear. When the internal fluid pressure in very thick cylinders reaches a certain critical figure, the material at the inner surface of the wall becomes overstrained and a certain amount of plastic flow takes place. This overstrain causes "work-hardening" of the inside layer of the wall, and this produces a skin of metal with a considerably higher elastic limit. Until the internal fluid pressure is raised quite an appreciable amount beyond the previous critical value no further deformation takes place. (As will be seen later, advantage is taken of this increase in the elastic limit of the inner layer due to work-hardening in preparing several types of pressure vessel for arduous service.) With increasing internal pressure further deformation and work-hardening results, and the depth of overstrain is increased in proportion to the pressure. In the case of cylinders of considerable wall thickness, the internal pressure required to overstrain the whole wall of the vessel is considerably greater than that necessary to deform the bore, and surprisingly high pressures can be satisfactorily controlled so long as a fair proportion of the wall extending from the outside inwards is still in the elastic state. Failure will occur when this outer layer of elastic material becomes too thin to prevent free plastic flow of the more highly stressed inner layers, and hence as previously stated, actual rupture starts at the outside and travels inwards. It is probable that a time element will enter into this method of failure, analogous to the "creep" encountered in less highly stressed vessels exposed to elevated temperature.

The best type of steel to use for such highly stressed vessels is one of the following chemical composition:—

C	Si	P max.	S max.	Mn	Ni	Cr	Mo	Fe Remainder
0·3	0·2	0·035	0·035	0·6	2·5	0·6	0·6	per cent.

This material should be used in the hardened and tempered condition. After normalising, it is heated to 830° C. and cooled in oil, and then tempered by reheating to 600° C. and again cooling in oil. The mechanical properties obtained by this heat-treatment are:—

Yield Point. Tons/sq. ins.	*Ult. Tens.* Tons/sq. ins.	*Red. of Area.* Per cent.	*Elong. in 2 ins.* Per cent.	*Izod Impact.* Ft. lbs.
60	70	50	20	40

These tests refer to test pieces taken from a 1⅛ in. diameter forged bar taken in a longitudinal direction. Transverse test pieces taken from forged vessels would give similar results for the yield point and maximum strength, but the values for the other three items would be materially reduced. It is important to note that test pieces for vessels of this description should be taken in a transverse direction, and a suitable specification would give the above figures for yield point and maximum stress, with minimum values of 40 per cent. for reduction of area, 15 per cent. for elongation, and 25 ft.-lbs. for the impact test. (Tests all transverse.)

As an example of the steels Bridgman uses for high-pressure cylinders, he advocates the following chrome vanadium steel:—

Cr	Mn	C	Si	Va	S	P
0·93	0·68	0·51	0·23	0·18	0·01	0·008

This steel is a product of the electric furnace.

In preparing a cylinder for service at pressures from 12,000-20,000 atms., Bridgman first machines the bore a little under size, say $\frac{15}{32}$ in., for a hole of ½ in. finished diameter. The steel is then hardened and tempered to give a Brinell hardness of 400 or so. After tempering, the bore is subjected to "autofrettage," i.e. the hole is filled with lead and pressure is applied to the lead until the bore of the vessel takes a permanent set. This "autofrettage" (which is described in greater detail later) increases the yield point of the material at the bore of the vessel, and the amount of permanent deformation required depends upon the subsequent working pressure of the cylinder. After "autofrettage" the bore is reamered to the desired dimension, viz. ½ in.

At such high pressures, even with "autofrettage," the bore increases very slightly with use at internal pressures of 10,000 atms. or so, and this slow increase in dimension becomes more pronounced as the pressure rises. At pressures of 15,000-20,000 atms., of course, one must be prepared for a short life of such vessels.

Bridgman has published a considerable amount of work of a physical character (compressibilities, viscosities, etc.) at pressures over 12,000 atms., so that it can be definitely stated that such pressures are regularly obtainable with simple cylinders.

No doubt much of the success of Bridgman's high-pressure cylinders has been due to his practice of cold working the bore of such vessels before putting them into service. This practice (which is known as "autofrettage"), has been used for many years in the manufacture of guns.

The following extract from a modern text-book on ordnance is of considerable interest in this connection. (Reprinted by permission from "Ordnance and Gunnery," by Col. Earl McFarland, published by John Wiley & Sons, Inc., New York.)

Manufacture of Guns by the Cold Working Pressure.

In a compound cylinder, the hoop is said to be "shrunk" on the tube to exert an exterior pressure and produce compression in the inner walls of the tube when the system is at rest. Shortly before, and during the World War, the cold-working process of gun-making was devised to produce this compression without hoops. The method, as originally developed, was termed *autofrettage*, a French term which, literally translated, means self-hooping. The introduction of this process has been the most revolutionary step in gun manufacture since the inauguration of the built-up gun about 1885.

Instead of manufacturing guns by the built-up and wire-wrapped methods, the U.S. War Department has adopted the cold-working process for use wherever applicable. Guns and howitzers of from 37 mm. to 155 mm. have already been successfully manufactured by this process; and designs have been completed for manufacturing an 8-in., 50 cal. gun (to consist of a tube and a removable liner) by the same method.

The process consists essentially in taking a single cylinder with the interior diameter slightly less than the calibre desired, and subjecting it to an interior hydraulic pressure of from about 44,000 to

100,000 lbs. per sq. in. The stress due to the hydraulic pressure decreases outward, and the pressure is so determined that the fibres of the metal take a permanent set, the inner diameter being increased approximately 6 per cent.

The cold-working process increases the proportional limit and tensile strength of the metal, and decreases the elongation, the contraction of area, and the Charpy impact test. These changes in physical properties are a maximum at the bore and a minimum at the exterior. The modulus of elasticity of a forging that has been cold-worked is found to vary from approximately 23,000,000 lbs. per sq. in. at the inner surface to 28,000,000 lbs. per sq. in. at the exterior.

Guns are made by the cold-working process in a single piece; except that guns having a high muzzle velocity and tending to erode rapidly are made in two pieces: a tube, and a liner which can be removed and replaced in the field. The tube and the liner are cold-worked separately.

The percentage enlargement produced in a right cross-section by cold-working decreases from the bore to the exterior; when the thickness of wall is the same as the diameter of the bore, the percentage enlargement of the exterior diameter will be approximately one-eighth of the percentage enlargement of the bore.

The normal physical properties of typical forgings, after heat-treatment, but prior to cold-working, are :—

Proportional limit	60,000 lbs. per sq. in.
Ultimate strength	90,000 „ „
Elongation in 2 ins.	18 per cent.
Reduction in area	30 „
Charpy test (tensile)	24 ft.-lb.

According to the present practice at Watertown Arsenal, the forging, after it has been subjected to the autofrettage treatment, is thoroughly heated at a temperature as high as 400° C., to remove the strains incidental to the process of cold-working. The metal is then allowed to cool slowly. This heat-treatment is termed *soaking*. The forging produced is almost ideal for gun construction, having a high yield point at the bore and sufficient elasticity to withstand high powder pressure without permanent set. The physical properties of forgings that have been cold-worked and soaked are approximately :—

Proportional limit	83,000 lbs. per sq. in.
Ultimate strength	98,000 „ „
Elongation in 2 ins.	15 per cent.
Reduction in area	20 „
Charpy test (tensile)	12 ft.-lb.

The cold-working process puts the metal adjacent to the bore under an initial compression and the exterior metal under an initial tension ; this effect on the metal at the bore is similar to that produced by shrinking an exterior cylinder on a tube. The autofretted cylinder, deformed from its normal state by the cold-working, is turned down and bored to its finished size. Removal of metal from the bore and from the exterior of a forging that has been cold-worked relieves the initial compression of the bore proportionately to the amount of metal removed ; the amount of this relief caused by removal of metal from the bore is obviously much greater than from the removal of the same amount of metal from the exterior.

The subject of autofrettage has also received the very close attention of the authorities at Woolwich Arsenal and the results of many years' experience of this subject have been recently published by Major Macrae in a book " Overstrain of Metals," published in 1930 by H.M. Stationery Office.

Poulter of the Department of Physics, Iowa (U.S.A.) Wesleyan College, has also contributed several ingenious developments in the design of very high-pressure apparatus for physical work, and most of his work has been published in the *Physical Review* during the past few years.

For his high-pressure apparatus, Poulter uses a steel known as S.A.E. 3250 (manufactured by the Republic Steel Corporation), a typical analysis of which is as follows :—

C	Mn	P	S	Si	Ni	Cr
0·50	0·56	0·017	0·022	0·224	1·76	1·08

After machining the steel is normalised at 1600-1700° F., quenched in oil from 1450° F., and tempered in salt from 750° F. This treatment produces a Brinell of 445.

Poulter considers that there is a certain cylinder wall thickness, determined by the inside diameter of the cylinder and the steel from which it is constructed, beyond which additional thickness does not add to the pressure the cylinder will withstand, and further that this thickness is reached when the elongation of the steel on the inside surface of the cylinder wall reaches a point where cracks develop before much stress is produced in the steel near the outer surface. For the above nickel-chrome steel, Poulter states that with an inside diameter of 1·6 cm. the maximum strength is obtained with a wall thickness of perhaps less than 6 cm.

These remarks are, of course, in regard to simple cylinders, and Poulter agrees that autofrettage is helpful in this respect. He considers that a coaxial shell arrangement, i.e. shrinkage of one cylinder over another, will give a pressure cylinder capable of withstanding the highest pressures and is carrying out experiments on these lines.

For pistons of very high-pressure plant Poulter uses Rex AA or Rex AAA high-speed steel, suitably heat-treated to give a high hardness value. Naturally such steels are very brittle, and Poulter encloses such parts within a ductile tube to prevent personal injury in case of sudden fracture or crushing.

Other details of Poulter's technique will be noted in Fig. 85 (*Physical Review*, 1932, **40**, 860). The cylinder is made from S.A.E. 3250 (previously described) and is heat-treated to maximum tensile strength. The piston B is made from high-speed steel, and is guided by the cylindrical guide C. The pressure is obtained by forcing the piston down by means of a 200-ton hydraulic press. The housing G serves as a water jacket and as a protection against flying fragments in case of a burst. The cylinder is kept at constant temperature by circulating water from a thermostat round the high-pressure cylinder (in the space H) and in the platens of the hydraulic press.

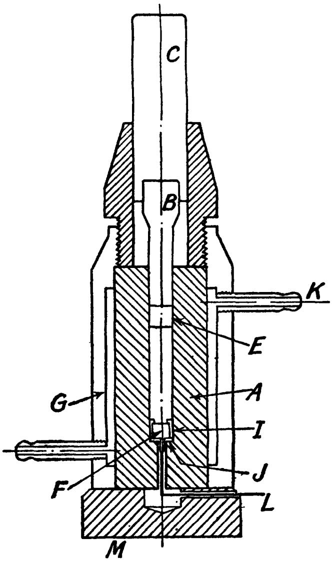


Fig. 85.—Poulter's cylinder for high pressures.

The body of the cylinder is machined from annealed steel allowing 0·005 to ·010 in. for grinding in the bore after heat-treatment. After the pistons have been heat-treated they are ground tight enough to require a pressure of 10-15 lbs. to force them into the cylinder. Leakage past the piston is prevented by placing a close-fitting good grade rubber stopper from 5 to 10 mm. in length, just ahead of the piston. (This type of packing has been used recently with success in the high-pressure laboratories of the I.C.I. at Northwich in the design of the intensifier for their 12,000 atm. autoclave (see Chapter V.))

In this type of cylinder (Fig. 85) the material under pressure is placed directly in the cylinder, and when an electrical connection is required a terminal is inserted through the bottom of the cylinder as shown in the figure. The hardened high-speed steel plug F is insulated from the sides of the cylinder by an enveloping shell of fibre I, and from the bottom end of the cylinder by a sheet of mica J about 0·5 mm. or less in thickness. The insulated wire L is soldered to the plug F, and is carried out through the hole in the bottom of the cylinder and through the groove in the base M. When the liquid in the cylinder is oil, such electrodes serve very well at pressures as high as 30,000 atms. and maintain a resistance of 300,000 ohms.

Poulter has also given considerable attention to the design and construction of a satisfactory window mounting for either glass or quartz windows for withstanding pressures as high as 30,000 atms. Amagat (1887-96) was one of the first investigators to design a satisfactory type of window, and this comprised a piece of glass in the form of a truncated cone with an enveloping cone of ivory as a jointing material between the glass and the steel wall. This window was then mounted in a tapered hole with the small end of the window outwards, so that the pressure in the vessel tended to keep the joint tight.

In the course of an investigation in Poulter's Laboratory it was found that glass capsules made from pyrex or soft glass tubing (6 mm. inside dia.) by sealing off the ends round would sometimes

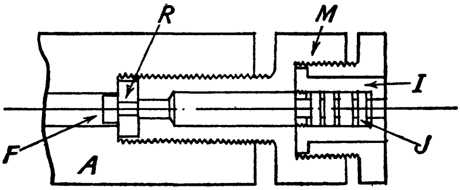


FIG. 86.—Poulter's design of window for high pressures.

withstand an external hydrostatic pressure of 12,000 atms. These capsules were about 20-30 mm. in length and had a wall thickness of about 1·5 mm. This led Poulter to believe that if a proper window support could be obtained it would be possible to use windows up to the highest obtainable pressures.

In carrying out experiments on very hard steel for the construction of pistons, samples of the steel ($\frac{1}{2}$ in. dia. × 1 in. long) were placed longitudinally between two blocks of hardened steel and pressure was then applied until the test pieces were crushed. With the thought that these steel cylinders would probably withstand a greater load if a thin sheet of soft steel were placed between the ends of the test pieces and the hardened steel blocks, sheets of soft steel 0·25 mm. thick were so placed. Contrary to expectations, under these conditions the test pieces were split at about one-half the load they had previously withstood.

Apparently, in this case the thin sheets of soft steel exerted lateral forces due to their flowing under pressure great enough to split the steel blocks. It seemed quite likely that failures of high-pressure vessel windows with gaskets was due to a similar cause. With this in mind, a window of the type shown in Fig. 86 was developed, in which the window F was mounted without a gasket and in contact with the polished surface of a very hard steel disc R about 10 mm. in thickness with a 6 mm. hole in the centre. This design proved quite tight at pressures sometimes as high as 30,000 atms. Safety windows J are fitted to catch flying fragments of the main window in case of sudden fracture, which, of course, must always be expected with such exceedingly high pressures.

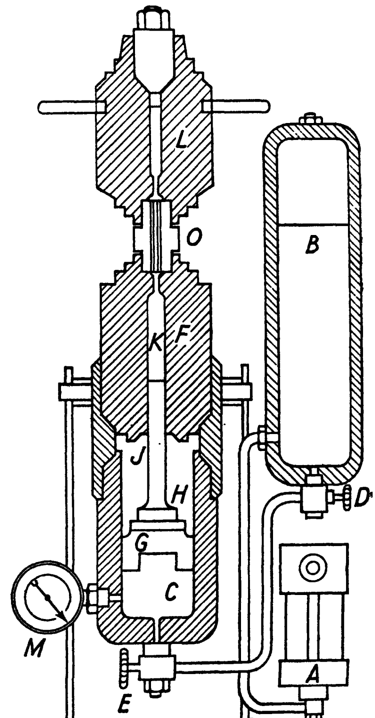


Fig. 87.—Basset's compression plant.

Professor Bone has recently published some work on explosions at pressures of 10,000 atms., in which he used a nickel-chrome-molybdenum steel cylinder reinforced by coil winding (*Proc. Roy. Soc.*, **A, 139,** 57). Apparently the method of construction was quite satisfactory.

A very interesting technique in very high pressures has been developed by M. James Basset of the Laboratoire des Recherches Scientifique aux Ultra Pressions, Paris. The first paper describing his work appeared in *Comptes Rendus* (1927, **185,** 344), and later papers are to be found in the same journal (1930, **191,** 928, and 1932 (Dec.), p. 1240).

The first paper (i.e. that appearing in 1927) described an apparatus for obtaining pressures of the order of 15,000 atms. when dealing with liquid media. Fig. 87 shows the details of the plant.

The hand hydraulic pump A is capable of supplying oil at a pressure of 1000 atms., and the oil at this pressure is stored in the accumulator B. The large cylinder C is supplied with the high pressure oil from the accumulator, and hence any liquid in the upper cylinder L is compressed to a pressure depending upon the ratio of the areas of the cylinders and upon the oil-pressure applied to the large piston. So that, neglecting friction, with an accumulator pressure of 1000 atms. and a ratio of diameters of the two cylinders of 20 : 1, the pressure obtainable in the cylinder L is 20,000 atms. Naturally friction cannot be wholly neglected, but Basset states that, thanks to great care exercised in construction and use, this is reduced to a negligible amount. Hence, as mentioned in Chapter V., Basset measures the pressure obtained in the small cylinder L by calculation involving the diameters and the pressure registered by the pressure gauge attached to the large cylinder.

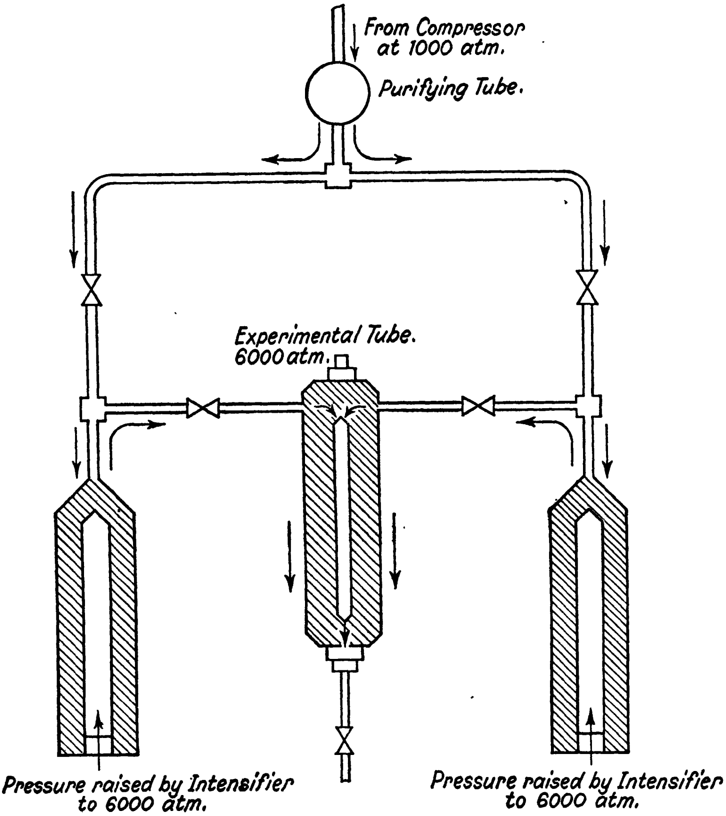


FIG. 89.—Basset's high-pressure circulatory plant.

The reaction chamber L is furnished with insulated electric leads, so that the liquid therein may be heated or subjected to electrolysis during application of pressure. The connecting tube O is made of several concentric tubes each shrunk on the preceding one. The internal diameter of this tube is 0·7 mm. and the outside diameter 22 mm.

Fig. 88 shows the general arrangement of the plant. The overall dimensions of the plant can be gauged from the height, which is 1·5 metres. The weight of the plant is about 300 kg. or 6 cwts.

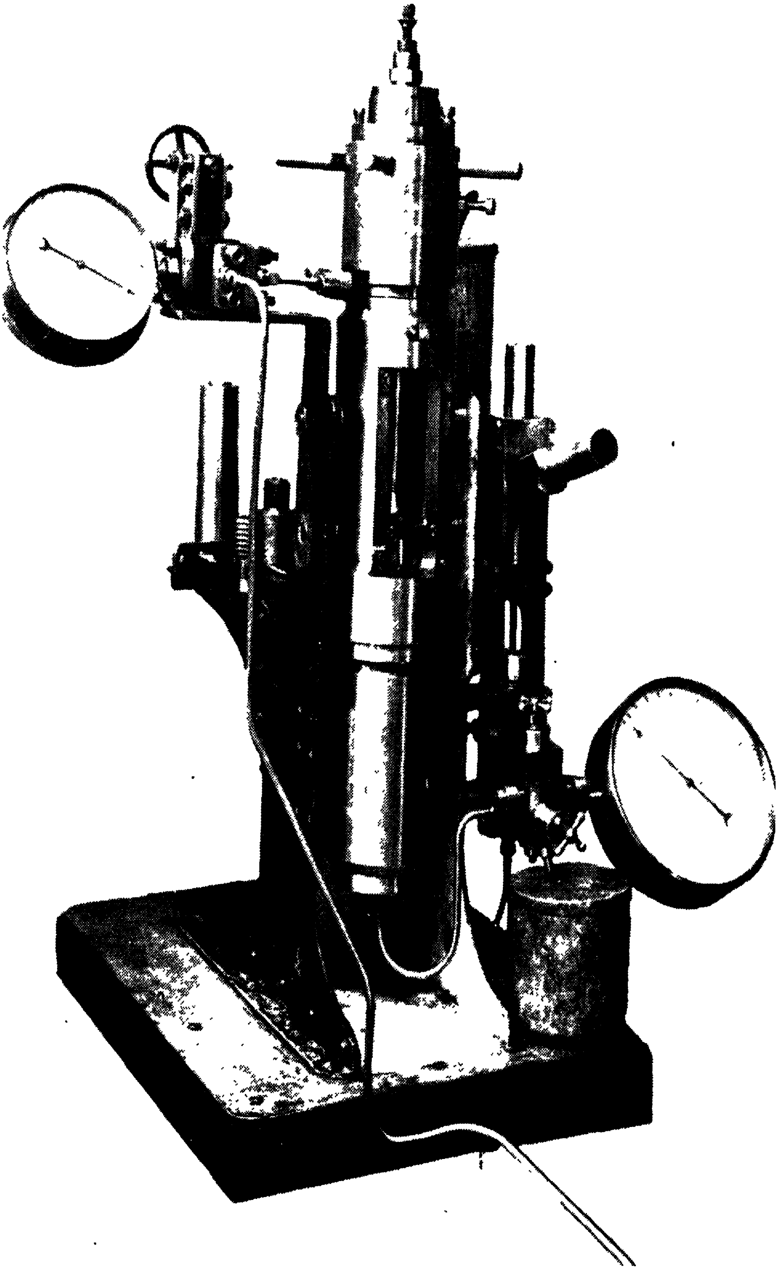


FIG. 88.—One unit of Basset's high-pressure plant.

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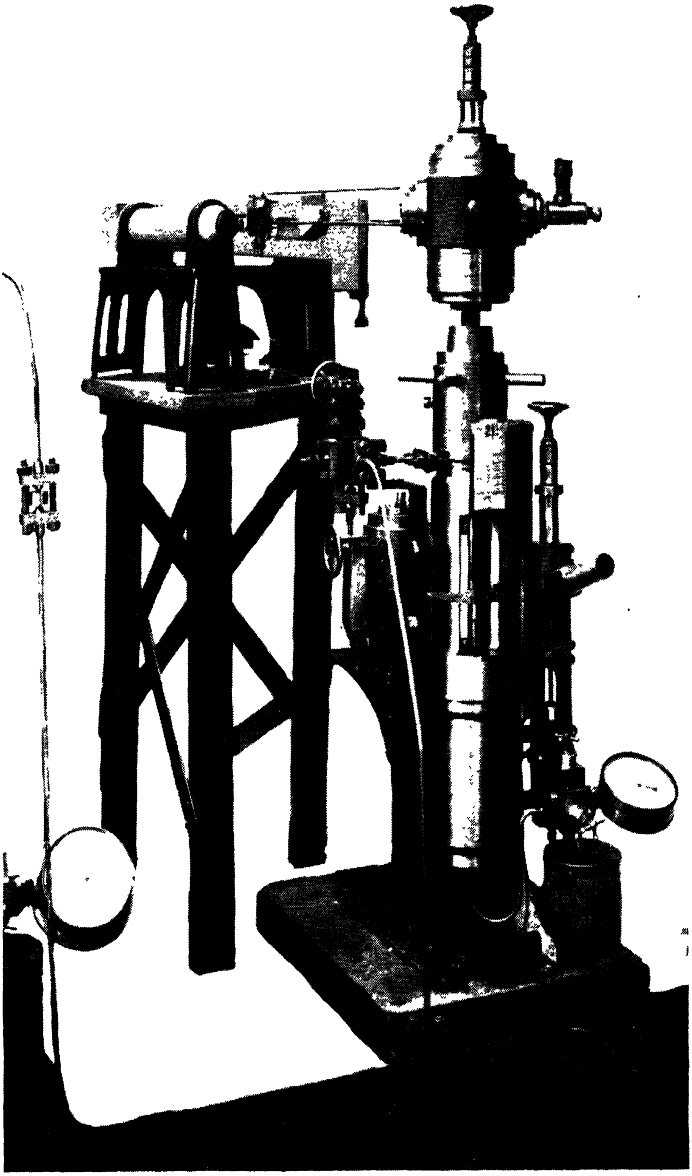

FIG. 90.—Basset's 15,000 atm. high-pressure vessel with sight glasses for inspection of interior of pressure vessel during an experiment.

[*To face page* 177.

It is to be noted that the above plant was designed and used for liquids. In the 1930 paper Basset published an account of an apparatus he had devised for use with gases and also an apparatus in which a gas or mixtures of gases could be passed continuously through the reaction tube, in which the internal temperature could be maintained at 1000° C., by means of internal heating, and at pressures as high as 6000 kg./cm.^{3}. The layout of this plant is shown in Fig. 89, and is self-explanatory. Note that the gas is supplied to the apparatus at 1000 atms. by a Luchard compressor, as described in Chapter II., and two intensifiers are used to pass the gas raised by intensification to 6000 atms. over the reaction tube.

Recently, in his 1932 paper, Basset describes a very ingenious method whereby he is able to examine visually gases or liquids when subjected to high pressure and temperature in the reaction tube.

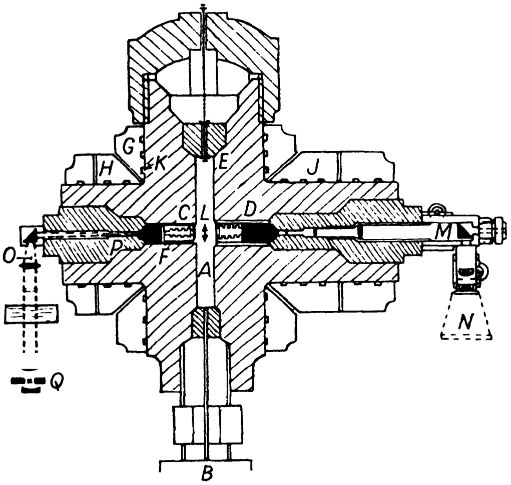

FIG. 91.—Basset's high-pressure vessel with windows.

The apparatus is adapted so that the material in the reaction tube may be also examined by a spectroscope, or a cinematograph film may be taken to show the course of events within the tube.

Fig. 90 shows the general arrangement of this latest plant. It is exactly as described for the ordinary reaction tube, except that this tube is fitted with side openings, as shown, to permit of the fitting of glass windows. The details of the reaction tube are shown in Fig. 91. The top opening of the reaction tube is fitted with an insulated electric lead for the heating current. The two side openings are fitted with hard glass windows. The cross form of reaction tube is fitted with four shrunk-on rings (G, H, J, etc.), which, in addition to giving mechanical stability, also form a water-jacket for cooling the walls of the tube.

The reaction tube in this case is 20 mm. diameter and 130 mm. long, and has been used for pressures as high as 15,000 atms.

A general view of the Basset Laboratory for high-pressure work is shown in Fig. 92.

So far, this discussion of the strength of cylinders exposed to pressure has been mainly confined to the shell of such cylinders. Naturally these shells must have some form or other of end closure, and the best form of end is hemispherical. It is not always possible to arrange this shape, and in fact in many cases a flat end-plate is necessary.

Regarding hemispherical end closure of cylinders, this ideal form is satisfactory if the thickness of the metal is not appreciably less than the thickness of the shell. The greater the departure of the shape of the end from this ideal form, the greater the thickness of metal necessary to withstand the pressure without undue distortion. So much depends upon particular conditions that it is impossible to state a general case, but examples of actual practice will be found in succeeding chapters.

The various members of a high-pressure plant are joined together by attachments involving the use of screw threads, and it is now proposed to deal with the strength of such threads, and notes as to their use in design.

Strength of Screw Threads.

In the first place, in pipe line fittings and valves, it is desirable to standardise on a thread such as the British Standard pipe thread, particulars of which are given on opposite page.

These threads are colloquially known in England as "Gas Threads," and are so described in the text and drawings in this book.

A very interesting series of experiments was carried out some years ago by Professor Dalby upon the strength of screw threads. (The results of these experiments are abstracted from "Strength and Structure of Steel and Other Metals," by W. E. Dalby, F.R.S., published by Edward Arnold & Co., and reproduced by permission of the author and publisher.) The experiments were devised to make comparison of strength between threads of different lengths, of different forms, and of different materials. He used two kinds of carbon steel (one containing 0·15 per cent. of carbon and the other 0·8 per cent. of carbon), and also brass, and he found that the way in which a thread fails depends on the material from which it is made. In hard steel, the plug thread sheared off near the root of the thread. In soft steel and plastic materials generally the threads failed as

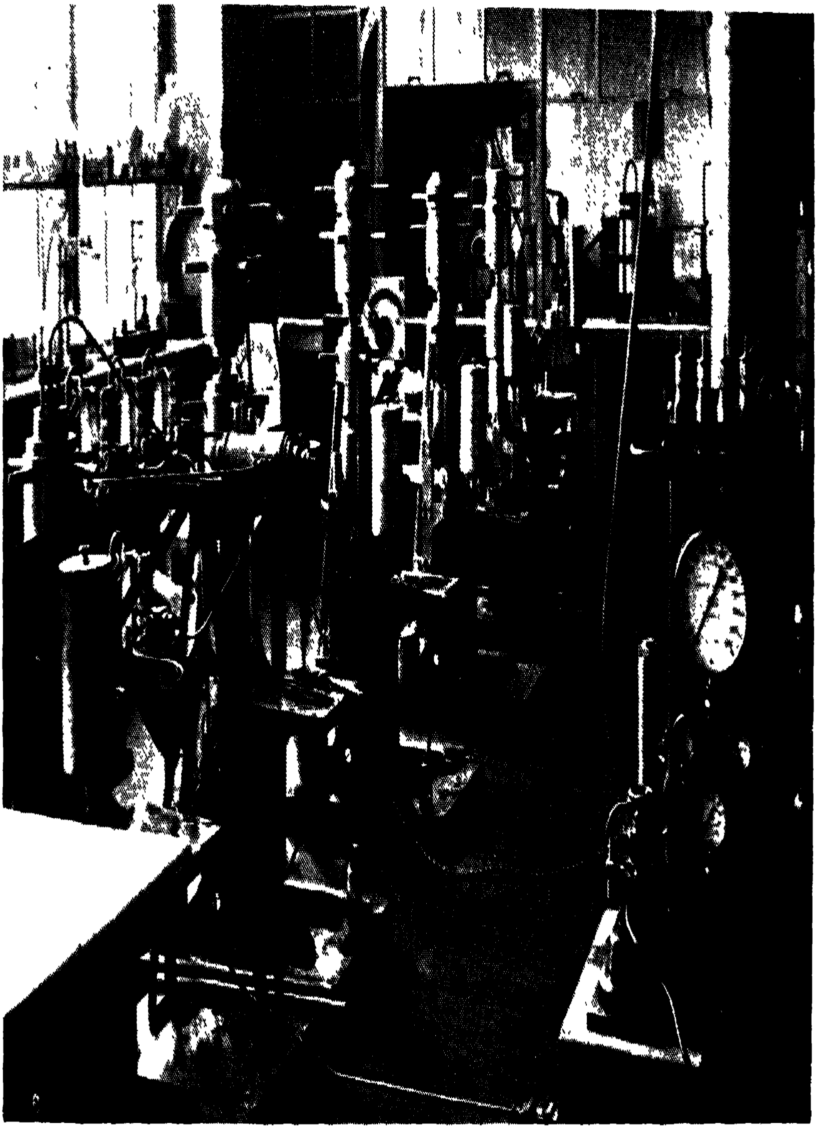

Fig. 92.—General view of Basset's high-pressure laboratory.

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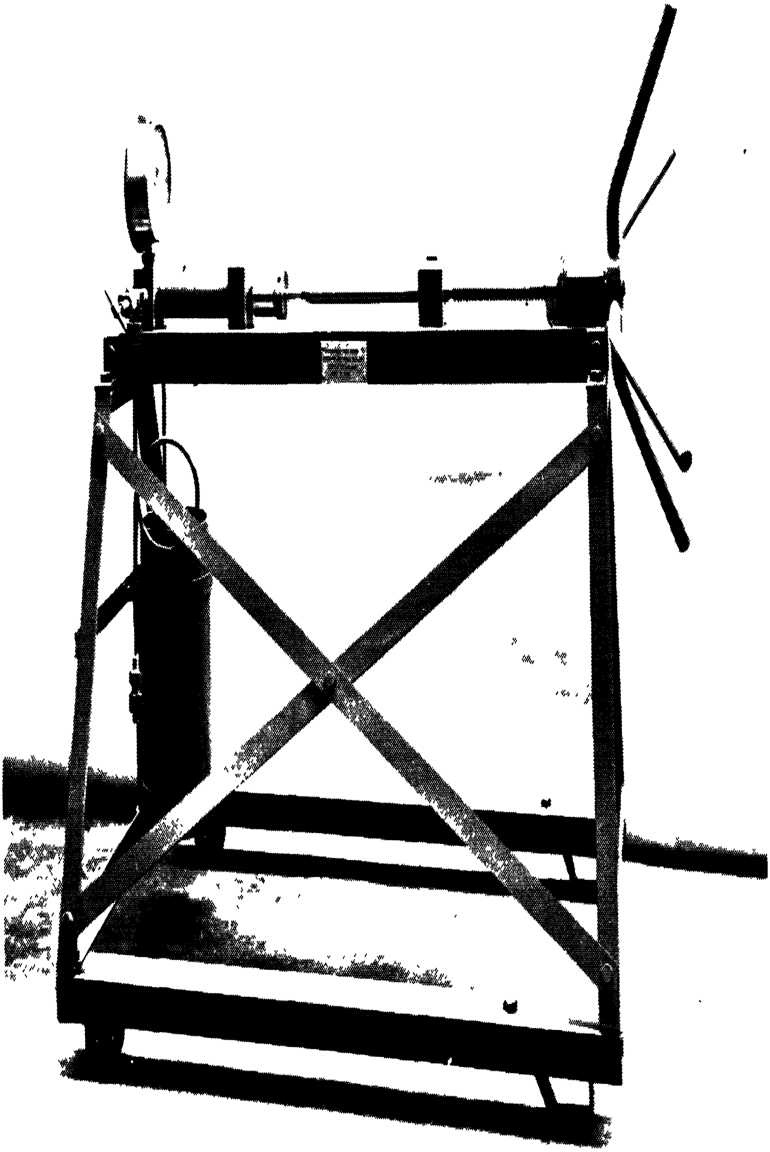

FIG. 95.—Chemical Research Laboratory hydraulic test pumps for 500 atms.

[*See page* 182.

British Standard Pipe Threads.

Bore of Tube. Inches.	Top Diameter of Thread. Inches.	Core Diameter of Thread. Inches.	No. of Threads. Per inch.
⅛	·383	·337	28
¼	·518	·451	19
⅜	·656	·589	19
½	·825	·734	14
⅝	·902	·811	14
¾	1·041	·950	14
⅞	1·189	1·098	14
1	1·309	1·193	11
1¼	1·650	1·534	11
1½	1·882	1·766	11
1¾	2·116	2·000	11
2	2·347	2·231	11
2¼	2·587	2·471	11
2½	2·960	2·844	11
3	3·460	3·344	11
3½	3·950	3·834	11
4	4·450	4·334	11
5	5·450	5·334	11

cantilevers, the plug threads turning up and the nut threads turning down until the deformed plug threads were pulled out by sliding over the deformed threads.

Professor Dalby used a screw of the following dimensions :—

1. Experimental part of screw ·625-in. diameter, and fourteen threads per in. turned to an equal number of threads.
2. Thread was turned on the end of a shank ½-in. diameter and ⅞-in. long.
3. The end of the specimen remote from the experimental screwed part was enlarged to 1-in. gas.
4. The test carried out in a tensile test machine.

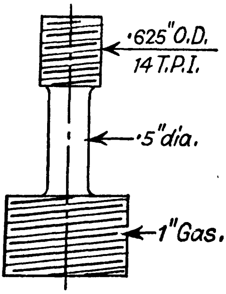

Fig. 93.—Test piece used by Dalby.

Test pieces were prepared (the sketch, Fig. 93, shows the form of the test piece) with 1, 2, 3, 4 and 5 complete threads as the experimental screw, and so far as the 0·15 carbon steel is concerned, it was found in the case of the specimens with 1, 2 and 3 threads that failure occurred by shearing of the threads. In the case of the 4-thread specimen, it failed by failure of the shank, but the threads were very badly distorted. In the case of the 5-thread specimen failure occurred by fracture of the shank.

Somewhat similar results, in so far as the number of threads required to prevent failure by shearing of the threads is concerned, were found in the case of the higher carbon steel and the brass.

Regarding thread form, the experiments show that the standard Whitworth form (angle 55°) is a little weaker than the 60° forms of thread, but there is so little difference that it is of no practical importance.

From the foregoing it will be clear that in calculating the stress in screw threads of parts subjected to a tensile stress, it is quite safe to base the design upon the area of the core diameter of the screw, provided that the length of the thread is not less than 90 per cent. of the diameter of the screw.

Apart from the actual stress in screw threads due to the working conditions, it is advisable to make an allowance in respect of "tightening-up" stresses. There is always a tendency to tighten stud nuts and screw plugs a little more than is necessary, and due allowance must be made for this in assessing the actual stress in the thread. I always make the following allowance in this connection :—

Screw Thread Diameter.	*Assumed Additional "Tightening up" Stress.*
$\frac{7}{8}$ in. to $1\frac{1}{8}$ ins.	50 per cent.
$1\frac{1}{4}$ ins. to $1\frac{5}{8}$ ins.	40 ,,
$1\frac{3}{4}$ ins. to $2\frac{1}{8}$ ins.	30 ,,
$2\frac{1}{8}$ ins. to $2\frac{1}{2}$ ins.	25 ,,
Over $2\frac{1}{2}$ ins.	20 ,,

Standard types of spanners should be used in all cases where plugs or cover plates are frequently removed, so that the "tightening-up" stress is uniform.

Several examples will now be given of the application of screw threads to high-pressure work. In the first instance, consider the plug closing the end of the 550 atms. gas bottle in Fig. 84. It is required to find the stress in this plug. The thread is $1\frac{1}{2}$-in. B.S.F., the core diameter of which is 1·34 ins. The cross-sectional area at the bottom of the thread is 1·41 sq. ins. Now it is assumed that the gas pressure tending to blow out the plug acts upon the whole area of the joint face, which is 2-in. diameter, and area therefore 3·14 sq. ins. The total pressure acting upon the plug on the above assumption is therefore 3·14 × 3·7 tons = 11·5 tons. The area resisting this pressure is 1·41 sq. ins.,* and therefore the stress on the plug is 8·2 tons per sq. in. As previously discussed, the stress is more than that by an amount corresponding to the force exerted in tightening down on the copper washer. According to the table, an allowance of 40 per cent. additional stress must be recognised on this account, and therefore it is concluded that a stress of 8·2 + (0·4 × 8·2) = 11·5 tons per sq. ins. is a fair estimate of actual conditions.

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* *See third paragraph above.*

Since the material used is heat-treated V. 30 Vibrac steel, with an ultimate strength of 55 tons per sq. in., there is an ample factor of safety.

For securing the end of large gas bottles, receivers, reaction vessels, etc., it is frequently necessary to use heavy flanges secured by bolts or studs. For such purposes, bolts or studs below $\frac{7}{8}$-in. diameter are not recommended, because in the smaller sizes the tightening-up stresses may easily be greater than the stress due to the working pressure, with obvious results.

As a case in point take the design of cover plate for a vessel for gas at 250 atms., as shown in Fig. 94. The material throughout is V. 30 Vibrac steel, and the joint between the cover and body is made on a copper washer which is retained between the two spigots. There are eight $\frac{7}{8}$-in. Whitworth studs and nuts to secure the cover, and the pressure of 250 atms. (1·67 tons per sq. in.) is assumed to act on the area enclosed by the outer circumference of the joint ring, which is $3\frac{3}{4}$-in. diameter, or an area of 11·04 sq. ins. The pressure on the end-plate due to the external pressure is therefore (1·67 × 11·04) = 18·5 tons. This pressure is taken by eight studs, and the pressure per stud is thus 2·3 tons. The area at the bottom of the thread of a $\frac{7}{8}$-in. Whitworth bolt is 0·422 sq. in., and therefore the stress in these bolts due to the pressure is 5·45 tons per sq. in. Again, assuming 50 per cent. additional stress in tightening up, we get a stress of 8·2 tons per sq. in., which is quite a reasonable figure.

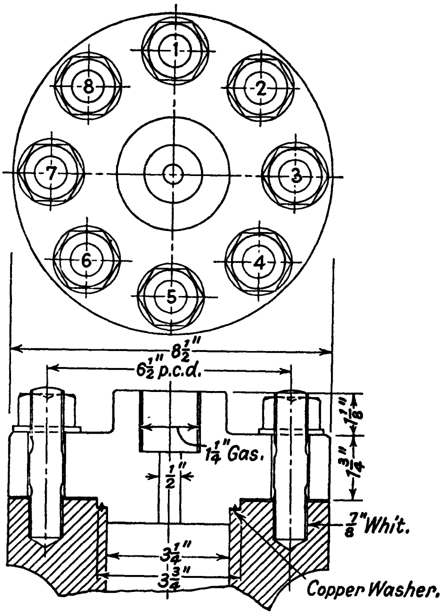

FIG. 94.

It will be noted that the thread of these studs is cleared away to the core diameter at the bottom of the thread. The object of this is to minimise the risk of fracture which is liable to occur at the end of the thread in highly stressed bolts if the bolt is parallel throughout. It is quite standard practice, and should be used in all such cases.

It will also be seen that there is a boss on the top of the cover plate. The object of this is to strengthen the end-plate, which would otherwise be weakened by the centre hole, and it is well to arrange that the volume of metal in the boss shall, as far as possible, be equal to, or greater than, the volume of metal removed by the hole.

Regarding the depth of the studs in the body, it is advisable to have this made (diameter of screw + ⅛d.) to give stability. In using high tensile steel, it is always advisable to tap with ground thread taps and screw the studs on centres in a good lathe. This ensures good mating of the threads, which is essential if binding is to be avoided. A little graphite and oil mixed is an excellent lubricant for the studs and nuts.

In designing covers for vessels of this character it is advisable to arrange the number of studs to be 4 or a multiple of 4. Then, in pulling down the end-plate in the case of, say, eight studs, one would tighten 1 and 2 lightly, then 6 and 5, then 7 and 8, then 4 and 3, resuming at 1 and 2 again, and so on, pulling down on opposite sides until the joint is made. Then, finally, I usually advise going round the studs in a clockwise direction, giving just that little extra "nip" so essential to preserve gas tightness for long periods. Each pair of bolts and nuts, or studs and nuts, should be similarly numbered, so that the same nut is always used on a given bolt or stud.

Regarding pitch and types of thread for studs and bolts, I always recommend ⅞-in. Whitworth as the smallest permissible size, and then above that it is advisable to use B.S.F. (British Standard Fine) threads. With a coarse pitch it is difficult to pull down a cover with the desired delicacy of touch and the B.S.F. threads are therefore used in the larger sizes.

Hydraulic Test.

Before putting into service all pressure vessels and fittings should be subjected to an hydraulic test to a pressure in excess of the working pressure. Great care is necessary in fixing the hydraulic test pressure, as this must in no circumstances approach the yield point of the material. This recommendation does not apply to vessels working at pressures much above 2000 atms., as the yield point is, of course, reached at pressures very little above the working pressure, and in any case, this point has already been dealt with under "autofrettage." An hydraulic test pump designed and built at the Chemical Research Laboratory for test pressures not exceeding 500 atms. is shown in Figs. 95 and 96. It comprises a plain cylinder with hand-operated valves of the type described in Fig. 136, and a simple plunger $\frac{1}{2}$-in. in diameter, which is operated by a capstan and screw. To test a pressure vessel, the pump is coupled to the vessel, and after care has been taken to eliminate all air and fill the system completely with water, a few strokes of the piston (withdrawing water from the tank and pushing it into the system) are quite sufficient to raise the pressure to 500 atms., even in the case of large vessels, say 20 litres capacity.

During hydraulic test, all flat surfaces, such as end-plates, should be carefully gauged for breathing, and noted for any permanent set. Also all significant diameters should be carefully measured before, during, and after the test. The procedure in the case of ordinary gas bottles has, of course, already been described by reference to the British Standard Specification for these vessels, and the procedure now suggested refers to vessels not adaptable for testing by the water jacket method or where facilities for such test are not available.

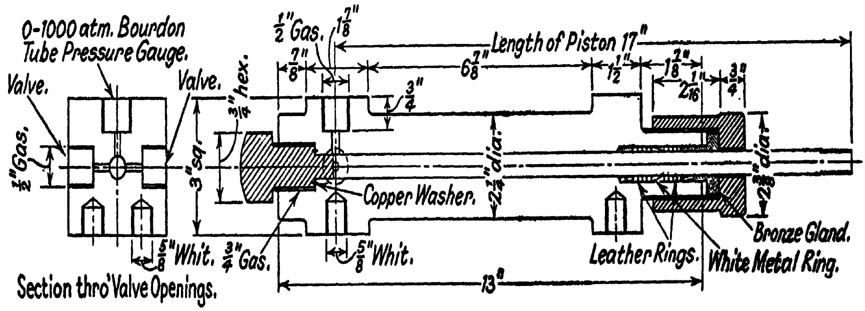

FIG. 96.—Cylinder of 500 atm. hydraulic test pump.

A log record should be kept for each pressure vessel, with particulars such as drawing number, overall size, working pressure, initial test pressure, and details of all uses to which the vessel is put. Pressure vessels should be regularly and thoroughly examined, periodically hydraulically tested, and the least defect thoroughly investigated.

As an example of the amount of elastic stretch when hydraulically testing large vessels, subjected to a test pressure of 500 atms., the 3 cu. ft. capacity gas bottles described on page 163 stretched by an amount equal to 25·0 cu. ins. There was no permanent set.

CHAPTER V.

MEASUREMENT OF PRESSURE.

In connection with pressure vessels, probably the earliest method of pressure measurement employed was the mercury column, such as was used by James Watt, and later by George Stephenson on the "Rocket." The mercury column is perhaps the most accurate of all pressure gauges, and it has been used by Amagat and Cailletet for pressures as high as 300 kg. cm.^{2}. There are several corrections to make in using such a gauge when used at high pressures, notably the compressibility of mercury and for the difference of the temperature at various parts of the column. An interesting account of the mercury column used by Michels in calibrating his "free piston" type of gauge, and the corrections necessary with mercury columns, is given in "The Calibration of a Pressure Balance in Absolute Units," A. Michels, *Proc. Roy. Soc., Amsterdam,* 1932, **35**, 994. For practical purposes, however, the mercury column gauge is impossible, and secondary gauges of the Bourdon tube or Schaffer diaphragm type were developed. To-day such gauges are made with a fairly high degree of accuracy and reliability. The Bourdon tube consists of a flattened tube bent into the arc of a circle (see Fig. 97), which, when pressure is applied internally uncoils slightly, and the movement is reproduced on a dial by a multiplying mechanism (see Fig. 98). The tubes are made from the finest quality octagonal steel. They are first bored and turned full length, then turned on the outside to give a perfectly even thickness of wall. At both ends of the tube threads are cut, and at the extremities there is formed a sharp edge which makes a metallic joint in boss and end-piece when the tube is screwed into position. The tubes are next bent to shape, hardened and tempered. Finally each tube is subjected to a careful examination and test.

In most experiments of a chemical nature, when the accuracy of pressure measurement is rarely required to a degree greater than 2 or 3 per cent., the Bourdon tube type of gauge is quite satisfactory for pressures as high as 1500 atms. or so. By "chemical experiments" I mean such as are customarily carried out in autoclaves or circulatory high-pressure plants.

Fig. 99 shows a Bourdon pressure gauge fitted with electric contacts which are caused to operate warning devices when pressures registered by the gauge reach maximum or minimum points.

Fig. 100 shows a Bourdon pressure gauge arranged for reproduction of the gauge readings at a distance, by electrical means. In this way, for example, the readings from a number of gauges scattered about an extensive plant can be readily brought to one central control or observation panel. The transmitter, as fitted to the back of the Bourdon tube gauge, consists of a rotor having very fine resistance windings arranged parallel to its axis, and is mounted on the gauge spindle which projects through the back of the gauge case. Under pressure variations the gauge spindle turns this rotor and varies the resistance in circuit with a spring bush which rests very lightly on its windings. These variations in resistance are transmitted to the indicator, which through them indicates the readings on the dial gauge. The indicator is a sensitive moving-coil galvanometer having a balanced system which neutralises any variations in the battery voltage, and so indicates with accuracy even when the battery is nearly exhausted. One indicator may be used for indicating any number of pressures by connecting any number of trans-

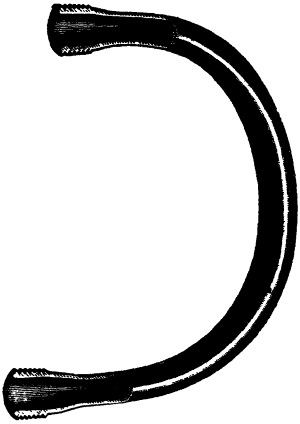

Fig. 97.—Bourdon tube for pressure gauges.

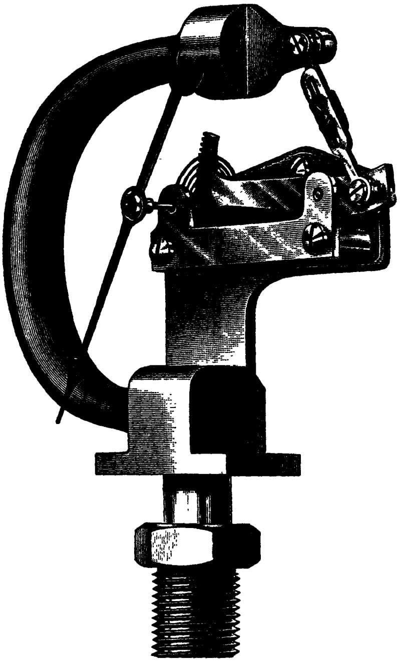

Fig. 98.—Mechanism of Bourdon tube gauges.

(Budenberg Gauge Co., Ltd.)

mitters to one switchboard and bringing any one of them into circuit as desired.

This system also lends itself to the distant graphic registration of pressures on continuous charts.

Above 1500 atms. or so, Bourdon tube gauges are definitely unreliable, and the unreliability increases rapidly with the pressure range. In such circumstances recourse may be had to the method used by Basset (*Comptes Rendus*, 1930, **191**, 925) in which he reduces the intensity of pressure by means of a reversed intensifier and measures the reduced pressure with an ordinary Bourdon tube gauge. Assuming no friction, the intensity of pressures is inversely proportional to the piston areas, and the diagram (Fig. 101) will clarify this. The high-pressure piston is (2) and the low-pressure piston is marked (3). The fluid pressure in the high-pressure cylinder (1) is found by multiplying the reading on the pressure gauge by the ratio of the areas of the large and small pistons. Unfortunately the friction of such devices is a variable quantity, and the method is at best but a rough approximation.

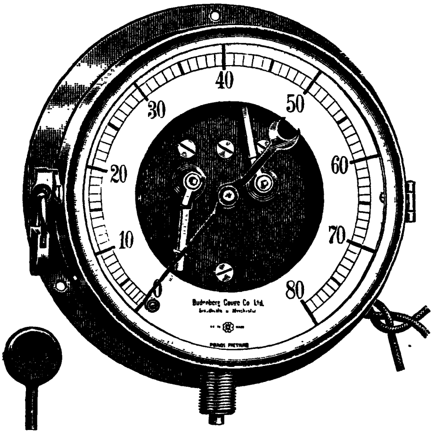

FIG. 99.—Bourdon pressure gauge with electric contacts.

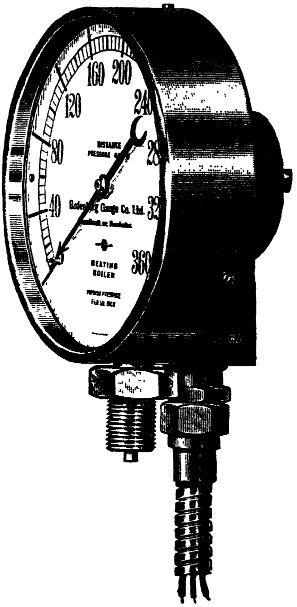

FIG. 100.—Gauge fitted with reproduction mechanism.

(Budenberg Gauge Co., Ltd.)

A successful secondary method of measuring very high pressure is that used by Bridgman. After a long series of experiments, he developed the manganin gauge, which was first introduced by Lisell. The electrical resistance of manganin increases with external pressure, and furthermore, the increase is practically linear. A further advantage of this material is that the temperature coefficient is low. Such resistance gauges for pressures as high as 2500 atms. are now made commercially by Kipp & Zonen of Delft, Holland, whose designs are based on the excellent work in connection with the accurate measurement of high pressure by A. Michels, of the University of Amsterdam. In the design marketed by Kipp, to eliminate the small temperature coefficient the resistance is measured in comparison with that of a second manganin wire kept at the same temperature. The coils of manganin wire are wound non-inductively on a porcelain cylinder in which deep grooves are cut, thus avoiding any strain on the wires.

The manganin gauge has been shown by direct measurement to be linear up to 13,000 kg./sq. cm. Bridgman has used it by extrapolation up to 21,000 kg./sq. cm.

The Bourdon tube gauge and the manganin gauge are, of course, secondary gauges, and must be calibrated in the first instance by some form of primary gauge. The mercury column is used by many firms making industrial types of Bourdon gauge for pressures not exceeding 30-40 atms. as their standard, but for higher pressures a free piston gauge is used. This gauge was employed by Perkins nearly one hundred years ago, but Amagat was the first to employ it really extensively. In Amagat's form of the appliance, two pistons (one large and one small) are mounted coaxially, and the small one is exposed to the high pressure to be measured. The total pressure on the small piston is transmitted directly to the larger piston which is in connection with a free mercury column. In this way the large piston may be made so large that a pressure of several thousand kg./sq. cm. may be measured with a mercury column a few metres high. In use the friction of the pistons is reduced by giving them a rotatory motion immediately before each reading. Amagat used this gauge for pressures as high as 3000 kg./sq. cm. At higher pressures the leak past the high-pressure piston became prohibitive. Leakage was cut down as far as possible by using molasses as the working fluid.

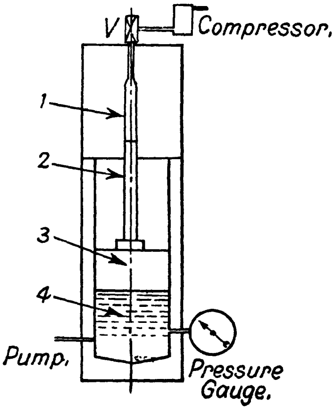

Fig. 101.—Basset's method for measuring high pressures.

Free piston gauges are now made commercially (marketed under the name of " Dead-weight testers ") and are used for the calibration of commercial Bourdon tube gauges where the pressures are higher than the range of the mercury manometer.

Dead-weight Testers.

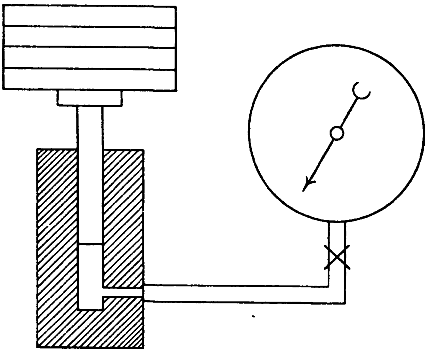

FIG. 102.

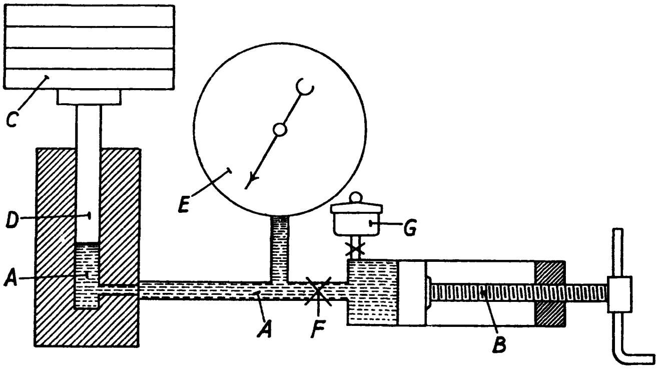

FIG. 103.

In nearly all dead-weight testers the principle is based on that of Amagat's free piston gauge, i.e. the pressure of a liquid (oil, glycerine, etc.) is balanced by the weight of a loaded piston floating in a cylinder. In its simplest form (Fig. 102) the dead-weight tester consists of a cylinder and piston only. The bottom of the cylinder communicates with a connection for carrying the pressure gauge (Bourdon, Schaffer diaphragm, etc.) under calibration. To use this type, the cylinder and connecting tube are filled with oil to a certain level. The piston is then inserted, and the weight laid on top. This type is now only used occasionally for quite low pressures. With this type, when calibrating large pressure gauges, it is often necessary to lock a certain quantity of oil in the gauge by closing the cock, and then lift out the piston in order to replenish the oil in the cylinder. To avoid this, all modern dead-weight testers are made, therefore, combined with a screw press and oil reservoir, so that the oil in the dead-weight system can be replenished without reaching the accurate dead-weight piston. Fig. 103 will make this quite clear. By means of the screw press the pressure can easily be regulated for carrying out tests of gauges at intermediate pressures, and also for testing or calibrating gauges against a higher pressure than that for which weights are available after the dead-weight portion has been cut off.

In every dead-weight tester it is necessary for the piston to be rotated freely in the cylinder to eliminate friction. Michels has done some very interesting work in this connection (A. Michels, *Ann. d. Phys.*, **72**, 285, 1923; **73**, 577, 1924). It is, of course, essential that the piston shall be a very close fit in the cylinder, and that it should rotate freely while readings are being taken. Also

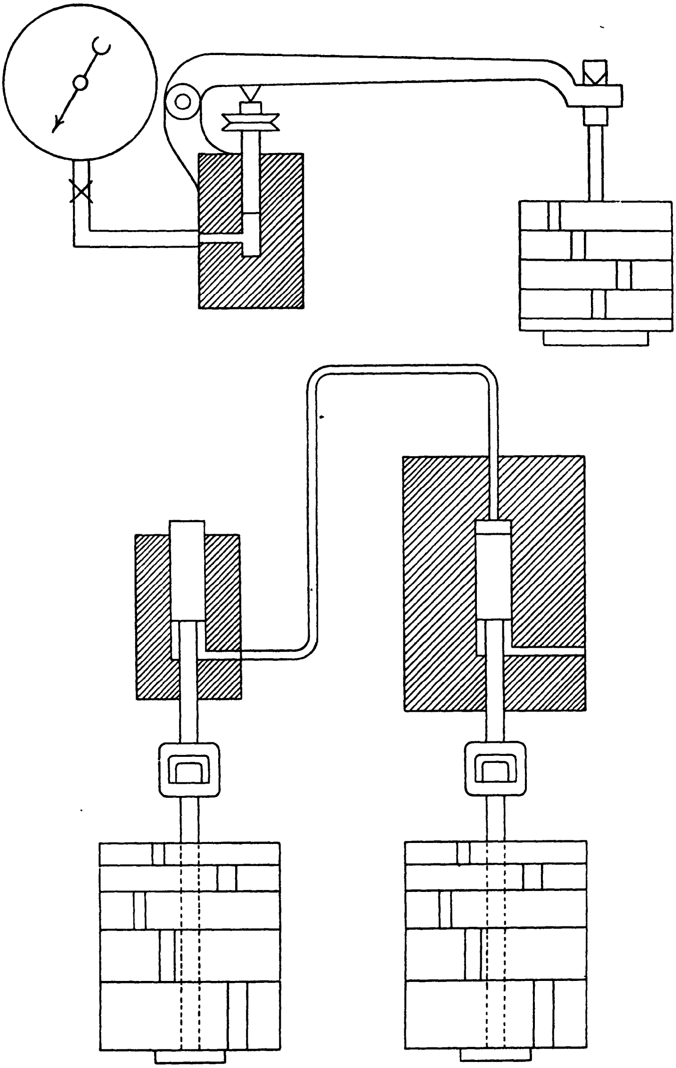

FIG. 104.—Differential tester dead-weight gauge.

the leakage of oil past the piston must be very minute, otherwise the pressure in a closed system at high pressure will rapidly drop.

As will be obvious when dead-weight testers are used for very high pressures, rather cumbersome heavy weights are required to balance the fluid pressure, and this renders the instrument unwieldy. To overcome this difficulty, and to avoid having an inconveniently small piston, many expedients have been tried, and are illustrated in Fig. 104 ; that is, the lever multiplying arrangement and the differential piston type. The first expedient rendered rotation of the dead-weight piston a little difficult.

The differential piston type has been developed by A. Michels of Amsterdam to a high degree of accuracy, and his designs are now marketed by Kipp & Zonen of Delft, Holland. Fig. 105 shows the Michels type of differential free piston gauge, which is made for pressures as high as 2500 atms.

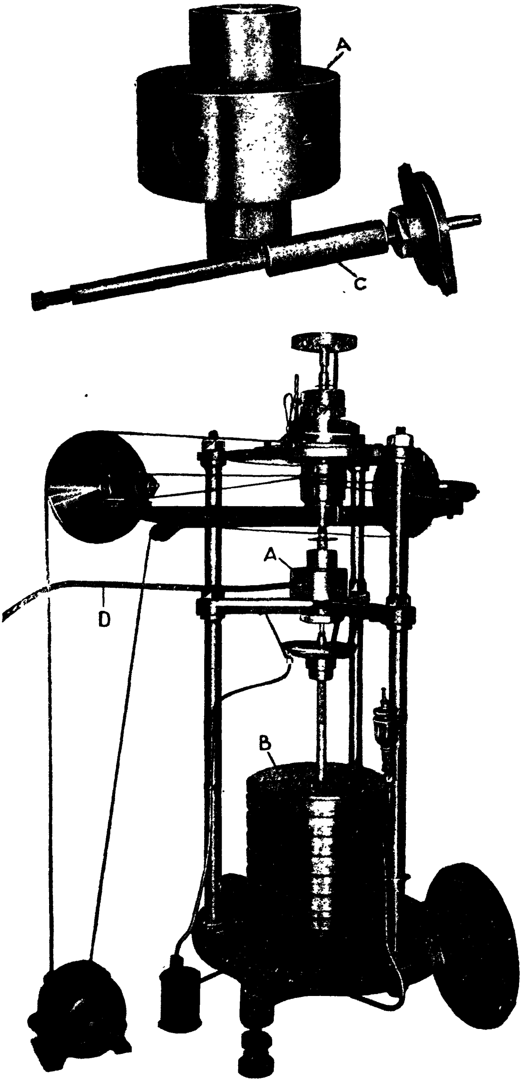

FIG. 105.

Fig. 106 shows one of the precision dead-weight testers made by the Budenberg Gauge Co., of Broadheath, near Manchester, for pressures not higher than 2000 lbs. per sq. in., and Fig. 107 shows a tester for pressures to 6000 lbs. per sq. in. In this tester a special design

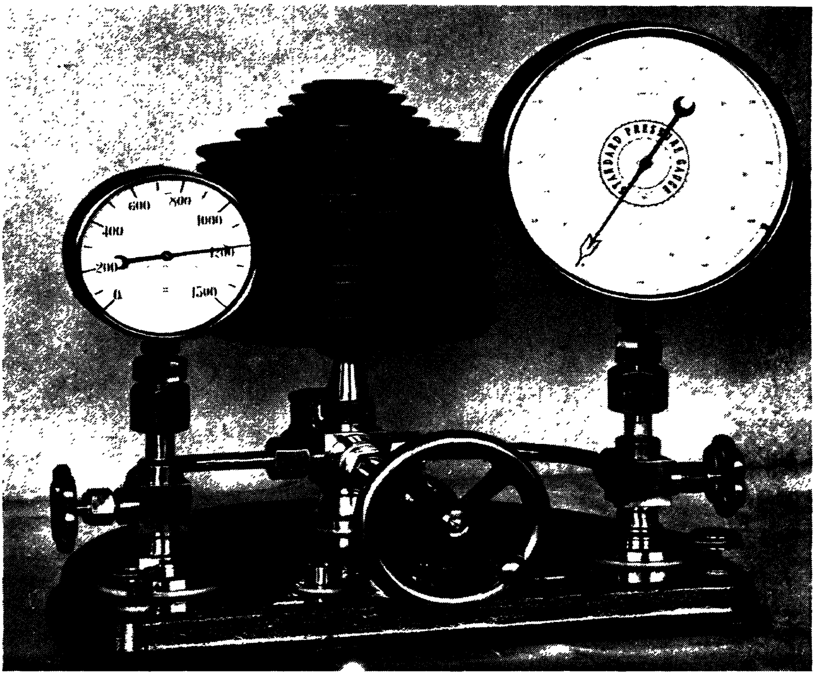

FIG. 106.—Budenberg 2000 lbs./sq. in. dead-weight tester.

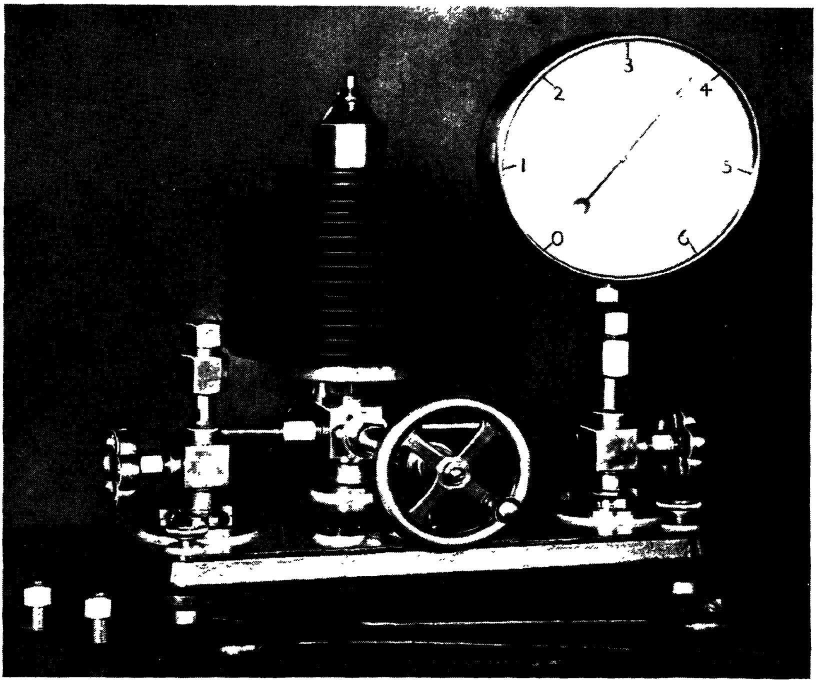

FIG. 107.—Budenberg 6000 lbs./sq. in. dead-weight tester.

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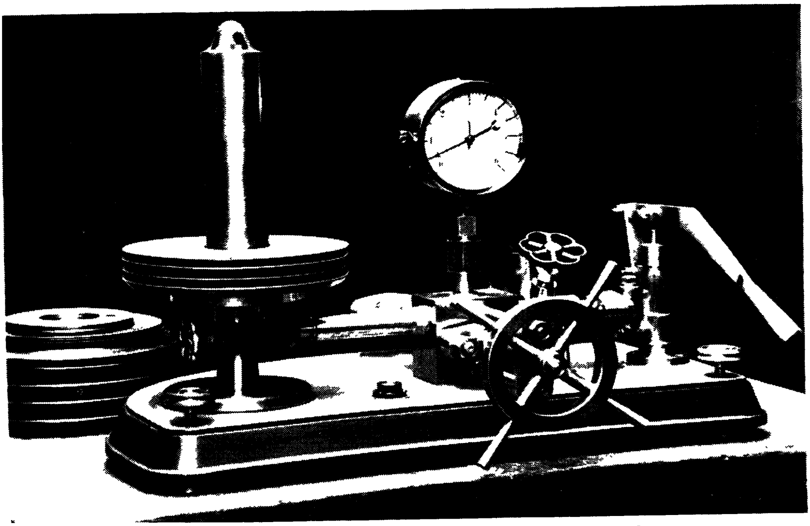


FIG. 108.—Budenberg 5-10 tons/sq. in. dead-weight tester.

[*See page* 191.

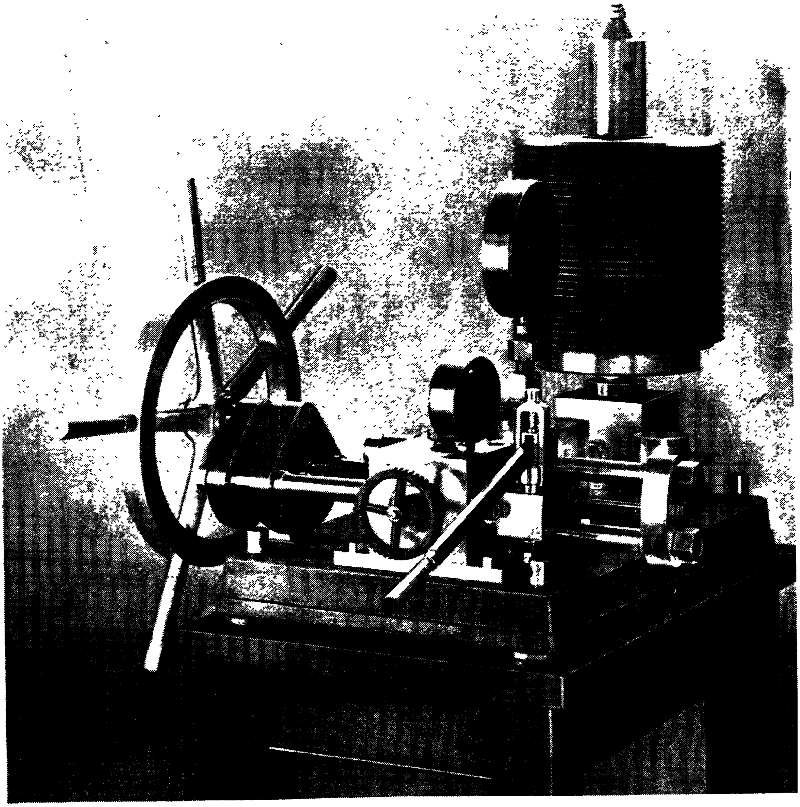


FIG. 109.—Budenberg 42 tons/sq. in. dead-weight tester.

[*To face page* 191.

of piston and cylinder and a novel method of carrying the weight have been used on the suggestion of the National Physical Laboratory. The area of the piston is ·02 sq. in. It is of glass-hard special alloy steel ground and lapped to within a few hundred thousandths of an inch of its nominal diameter—·15957 in. The weights are carried on a dome supported by a ball joint head on top of the piston. The ball allows the dome and weights to oscillate slightly so as to avoid all side stresses on the piston, whilst ensuring that the force of the weights is applied coaxially with the piston.

Fig. 108 illustrates a Budenberg precision high-pressure tester for pressures of 5 or 10 tons per sq. in. The dead-weight part proper shown on the left consists of a pedestal of forged steel on a gun-metal base fitted with a release valve. The pedestal carries a stout pillar of steel into the top of which is screwed the cylinder. The cylinder is made of crucible cast steel hardened and lapped to a high degree of accuracy to fit the piston with a minimum of clearance. The piston is made of special alloy steel glass-hard and ground and lapped to a high degree of accuracy as regards diameter, roundness and straightness. The piston has a sectional area of 0·02 or 0·01 sq. in., according to the range of pressure for which the machine is intended. The weight carrier is loaded with a small balance weight to give a round starting figure, say 250 lbs. per sq. in. The carrier, balance weight and additional annular weights are machined all over and calibrated to within half a grain dead weight. The screw press body is of forged steel. Into it at the back is screwed a cylinder of fine crucible steel accurately bored, hardened and lapped, to fit the plunger which is also hardened, ground and lapped. The plunger is actuated by an acme threaded screw of chrome nickel steel, and rotated from the front in a stout bridge of polished steel, supported by pillars screwed into the main body of the press. The thrust on the spindle is taken up by a bearing in the main body. On the spindle is threaded a second and movable bridge of polished steel which, by means of two stout rods, acts on a third bridge to which the plunger is fixed. When the spindle is rotated clockwise by the handwheel the loose bridge at the back is pulled forward and the plunger is forced into the cylinder and vice versa. The hand pump on the right of the tester is used to give initial pressures of 500 or 1000 lbs. per sq. in. This pump has a gun-metal body, steel piston, connecting link and lever. The pump draws its oil from an oil container beneath the base of the machine, and the oil released by the valve at the foot of the dead-weight column is automatically returned to this container. A special feature of the design is that all main parts are secured to the base from underneath, the object being to keep the apparatus clean and tidy and to avoid projecting screwheads or bolts round which dirt and grime can collect.

A tester designed and built by the Budenberg Gauge Co. for pressures up to 42 tons per sq. in. is shown in Fig. 109. This machine is similar in principle to the one just described, but every detail has been specifically developed to suit the very high pressure to be measured. The body of the screw press and the base of the dead-weight gauge are forgings of high tensile alloy steel specially treated to obtain density and toughness. The screw of the press is geared down at a ratio of 2·5 : 1. The handwheel is 3-ft. diameter over the spokes. The cylinder of the screw press is made of carbon steel, hardened and lapped, and the piston of special alloy steel. The diameter of the piston of the screw press is 12·5 mm. (just under $\frac{1}{2}$-in.) and the stroke 120 mm. (about $4\frac{3}{4}$ ins.). The filling pump (see back view) is made entirely of forged steel finished bright all over, and the valves of this filling pump are spring loaded. By means of this filling pump initial pressures of 6-7 tons per sq. in. can be obtained.

A tall, stout steel pillar is mounted on the base and to the top of this the actual tester cylinder is screwed. It is claimed that the piston of this tester is " perfect " in that it is accurate to within 1/100,000 of nominal diameter (·11285 in.).

As the effective lift of this tester piston is only $\frac{1}{16}$ in. and the volume of oil required to float it is $\frac{1}{1600}$ cu. ins., i.e. the volume required to raise it from the position of rest to the working height, the actual flow or leakage of oil is extremely minute, even at the very high pressure of 42 tons per sq. in.

Bridgman has developed the free piston gauge for pressures as high as 13,000 atms. Fig. 110 shows the construction of such a gauge for these very high pressures, in which two definite methods of avoiding leakage are adopted. The piston is made very small in diameter, namely, $\frac{1}{16}$ in., and the cylinder in which the piston is working is so arranged that the pressure on the external surface assists tightness. This will be clear from the drawing. With such a gauge, Bridgman has secured accuracy of the order of 0·1 per cent. at the maximum working pressure, namely, 13,000 atms. In operation the piston is slowly rotated, and the liquid used is a mixture of equal parts of glycerine and water, with sufficient glucose to make the mixture into a rather thick syrup. Bridgman used this gauge in the calibration of his manganin resistance gauge, which he used in routine work because of its simplicity.

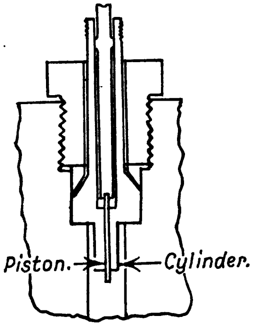


FIG. 110. — Bridgman's design of free piston pressure gauge.

Fig. 111 shows the method of connecting Bourdon tube gauges when the working pressure is not higher than 300 atms. The gauge shank is screwed $\frac{1}{2}$ in. gas and a ball nipple is screwed and brazed to the pipe line. A cap nut secures the ball nipple to the gauge shank as shown. This type of union is described more fully in Chapter VI., wherein will be found dimensions of the various parts.

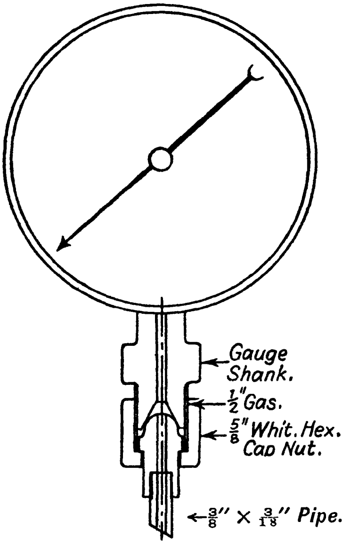

Gauge Shank.
$\frac{1}{2}$"Gas.
$\frac{5}{8}$"Whit. Hex. Cap Nut.
$\frac{3}{8}$" × $\frac{3}{18}$" Pipe.

FIG. 111.—Pressure gauge attachment to pipe line, 300 atms.

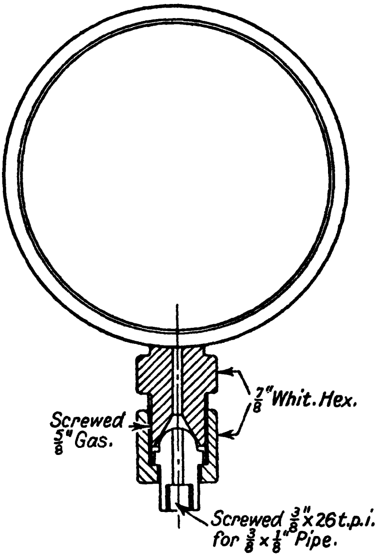

$\frac{7}{8}$"Whit. Hex.
Screwed $\frac{5}{8}$"Gas.
Screwed $\frac{3}{8}$"x 26 t.p.i. for $\frac{3}{8}$ x $\frac{1}{8}$"Pipe.

FIG. 112.—Gauge connection for 750 atm. pipe lines.

For pressures 300-750 atms. the arrangement shown in Fig. 112 is quite satisfactory. This is similar to the 300 atm. connection, but the various parts are appropriately strengthened. From 750-1500 atms. and 1500-3000 atms. the same type of connection is used, but the general dimensions in the latter case are increased (Fig. 113). The joint ring which may be of white metal or copper is trapped between the two diameters on the gauge shank. This type has been successfully used in the C.R.L. 3000 atm. plant described in Chapter VIII.

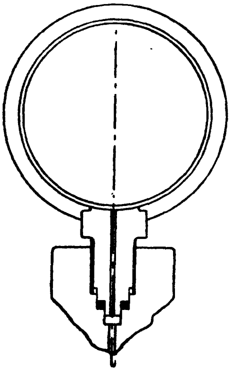


FIG. 113.—Gauge connection, 1500 atms.

All reputable manufacturers of Bourdon tube pressure gauges use great care in every stage of manufacture to ensure mechanical soundness, but at pressures over 50 atms. or so there is always a risk of a burst Bourdon tube, which may cause a serious accident. At the

Chemical Research Laboratory all such gauges are read by indirect methods, such as mirrors, etc., and the actual gauge is surrounded by a metal box. The back covers of all Bourdon gauges are fitted with explosion doors or canvas circles, and the fronts are fitted with triplex glass or celastoid, so that the effects of a burst are much minimised.

All laboratories using pressure gauges should have means whereby the accuracy of such gauges can be ascertained from time to time. A specially calibrated Bourdon gauge, kept as a standard for comparison, is perhaps the most convenient method, in which case the standard should be sent to the manufacturer periodically to ensure that the calibration is accurate.

As a general rule Bourdon tube gauges should not be used for pressures much greater than half the dial range. In other words, a gauge with a scale reading 0-500 atms. should rarely be used at pressures greater than 250 atms. This is standard practice in the case of boiler and similar plants.

CHAPTER VI.

PIPING, VALVES AND FITTINGS FOR HIGH-PRESSURE SERVICE AT ORDINARY TEMPERATURE.

THIS chapter deals with practical details such as pipework, valves, and fittings for high-pressure service.

Piping.

The piping used in high-pressure work may be solid drawn copper or mild steel, solid-drawn medium carbon or alloy steel, or it may be made by drilling a small hole through a bar of alloy steel for experimental work at the highest pressures.

When copper is permissible from the point of view of the effect upon the materials used in a physical or chemical experiment, solid-drawn tube of this metal is quite permissible for pressures as high as 550 atms. Some workers use copper tube for even higher pressures, but my experience with copper tube above 550 atms. has not been uniformly satisfactory.

For pressures up to 300 atms., solid-drawn seamless copper tube with ratio $\frac{D}{d} = 2$ is quite satisfactory (e.g. 2-in. outside diameter × 1-in. bore, ⅜-in. outside diameter × $\frac{3}{16}$-in. bore, etc.). For pressures between 300-550 atms., it is advisable to increase the wall thickness to give $\frac{D}{d} = 4$ (e.g. 1-in. outside diameter × ¼-in. bore, ½-in. outside diameter × ⅛-in. bore, etc.).

In cases where it is desired to use steel for pressures to 300 atms., solid-drawn mild steel tube with a ratio $\frac{D}{d} = 2$ is quite satisfactory (3 ins. × 1½-in. bore, etc.). From 300-750 atms. it is well to increase the ratio $\frac{D}{d}$ for mild steel to 3. From 750-1500 atms. chrome-molybdenum steel tube of ratio $\frac{D}{d} = 4$ is quite satisfactory. Above 1500 atms. it is preferable to use drilled alloy steel tubes, say ¾-in. outside diameter × ⅛-in. hole up to 2500 atms., 1⅛-in. outside diameter and ⅛-in. hole up to 5000 atms., and 1½-in. outside diameter × ⅛-in. hole to the highest obtainable pressures. Above

3000 atms. such tubes should be subjected to the autofrettage treatment.

There are no immediate commercial possibilities for the employment of pressures above 1000 atms., and all such plant is of an experimental character, in which the volumes handled are small. Such apparatus must necessarily be as compact as possible, hence pipe lines are rarely more than 1 ft. long, so that drilling a hole $\frac{1}{8}$-in. diameter through bars of this length is not a formidable task. Nickel-chromium-molybdenum steel is recommended for such tubes, heat-treated to give good ductibility.

As an example of American practice in experimental high-pressure work for pressures up to 1000 atms., the American Instrument Co. of Washington, D.C. (who are marketing a special line of high-pressure apparatus developed in conjunction with the Fixed Nitrogen Research Laboratory of the U.S. Department of Agriculture), recommend two sizes of tube. These are $\frac{1}{4}$ in. × $\frac{1}{16}$ in., and $\frac{9}{16}$ in. × $\frac{3}{16}$ in., made from solid-drawn chrome-molybdenum steel.

For passing small quantities of gas at pressures not exceeding 400 atms. where flexibility is desirable, Hofer recommends copper capillary tubes of 4 mm. outside diameter and 2·5 mm. bore.

As examples of special high-pressure solid-drawn steel tubes which are commercially available in this country, the following sizes are regularly made by Accles & Pollock of Oldbury, Birmingham :—

Mild Steel.

Inside Diameter. *Inch.*	*Outside Diameter.* *Inch.*
·004	$\frac{1}{8}$
·010	$\frac{3}{16}$
·020	$\frac{1}{4}$
·016	·394
·031	$\frac{3}{8}$
$\frac{1}{8}$	$\frac{11}{16}$
$\frac{3}{16}$	$\frac{3}{8}$
$\frac{1}{4}$	$\frac{1}{2}$

and many sizes of thick walled tubes of considerably larger outside diameter for commercial work with ratio of $\frac{D}{d}$ or $K = 2$ or 3, or as desired.

Alloy Steels.

This firm also manufactures a special range of small high-pressure tube, made from chrome-molybdenum steel of the following approximate chemical composition :—

Carbon	0·25 to 0·35 per cent.
Manganese	0·60 per cent max.
Silicon	0·30 ,, ,,
Sulphur	0·040 ,, ,,
Phosphorus	0·040 ,, ,,
Nickel	Nil.
Chromium	0·80 to 1·10 per cent.
Molybdenum	0·15 to 0·25 ,,

As a final operation, these alloy tubes are given the following heat-treatment :—

Normalised by heating to 900° C. and cooled in air.
Water quenched from 900° C.
Finally water quenched from 650° C.

Tubes from this alloy steel are made in the following standard sizes for experimental work, but larger sizes are available if desired :—

Inside Diameter. *Inch.*	*Outside Diameter.* *Inch.*
$\frac{1}{16}$	$\frac{1}{4}$
$\frac{1}{8}$	$\frac{3}{8}$
$\frac{1}{8}$	$\frac{1}{2}$
$\frac{1}{8}$	$\frac{5}{8}$

Accles & Pollock are also marketing a standard range of solid-drawn stainless tubes of many different sizes and types, including the well-known 18 : 8, the 15 : 11 chromium nickel and the 13 per cent. chromium classes.

Stainless steel tube is very useful in many parts of a high-pressure apparatus, but it is only recently that solid-drawn tubes of this material have become available. The sizes of this stainless steel tube for all ranges of pressure should correspond with the dimensions for carbon and alloy steels previously given. There are, of course, many grades and types of stainless steel on the market, and care should be taken to choose the most appropriate type for a specific duty. This point will be discussed more fully in a later chapter.

Pipe Fittings.

Regarding pipe unions and connections of pipes to pressure vessels, etc., there are different types to correspond with each kind of material used and the desired pressure range.

Fig. 114 shows an approved design for pipe union for $\frac{3}{8}$-in. × $\frac{3}{16}$-in. steel or copper pipes for pressures up to 300 atms. For copper pipes the union is made in bronze, and for steel pipes from mild steel. To attach the pipe to the union the former is screwed $\frac{3}{8}$ × 26 T.P.I., and screwed with soft solder to seal the joint in the case of copper pipes, and silver solder in the case of steel pipes. When soldering, the pipe should be screwed home when the solder is still fluid. so that a good gas-tight seal is obtained. The joint between the nipple and the body of the union is of the ball and cone type, in which the area of contact is quite small.

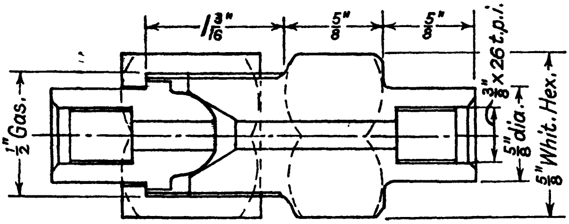


Fig. 114.—Pipe union, 300 atms. Bronze for copper pipe lines, steel for steel pipe lines.

Fig. 115 shows a tee-piece, and Fig. 116 a pipe manifold for taking several branches from a pipe line. Fig. 117 shows a cross suitable for the same pressure. These designs are suitable for 300 atms., and the dimensions of the various loose parts are all interchangeable with each other and those of the pipe union just described, so that alterations, extensions, renewals, etc., are greatly facilitated.

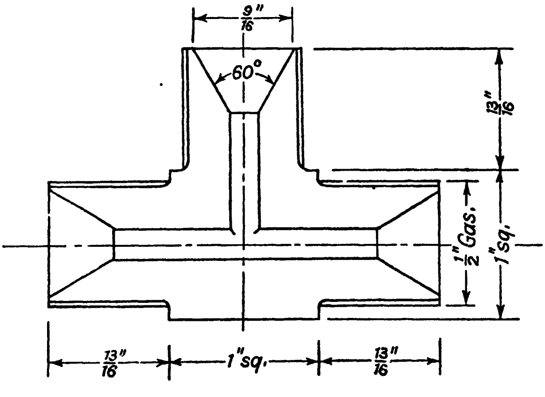


Fig. 115.—Tee-piece, 300 atms. Bronze for copper pipe lines, steel for steel pipe lines.

For ⅜-in. × ⅛-in. bore steel piping between 300 and 750 atms. the pipe union shown in Fig. 118 is quite suitable. It is very similar to the union just described for 300 atm., except that there are two nipples to each union body, and the parts are strengthened a little. Fig. 119 shows a method of attaching pipe lines to vessels, receivers, etc. One end of the nipple is turned flat and seats against a copper washer in the body of the vessel. Tees and manifolds for this higher pressure range are designed to be interchangeable with the unions, as in the case of the fittings for the lower pressure. Fig. 120 shows a pipe tee-piece for pressures between 750 and 1250 atms. The pipe ends are turned down to ·518 in. and screwed $\frac{1}{4}$ in. gas (nineteen threads per inch left hand). A coupling nut is brought home over a collar which is screwed on the pipe, and the pipe end, which is turned to 55° angle, is pulled against the 60° angle of the body of the tee-piece. Manifolds, unions, etc., are made on the same basis.

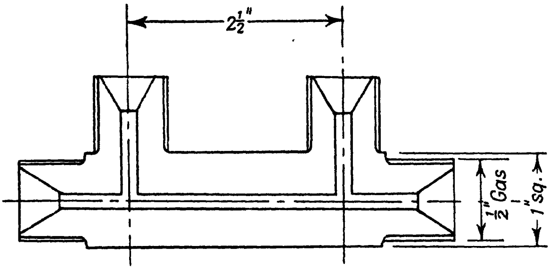


Fig. 116.—Pipe manifold, 300 atms. Bronze for copper pipe lines, steel for steel pipe lines.

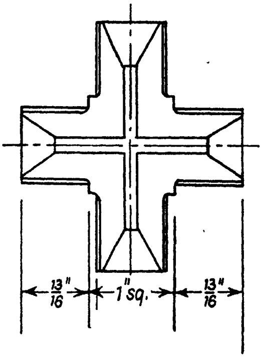


Fig. 117.—Cross-piece, 300 atms. Bronze for copper pipe lines, steel for steel pipe lines.

For their standard tube of $\frac{1}{4}$ in. × $\frac{1}{16}$ in. and $\frac{9}{16}$ in. × $\frac{3}{16}$ in. for pressures as high as 1000 atms., the American Instrument Co. supply pipe fittings of the type shown in Fig. 121. The drawings are self-explanatory, and it will be seen that these fittings are of the same general design as those in Fig. 120, but it will be noted that the cap nut goes inside the blocks instead of outside.

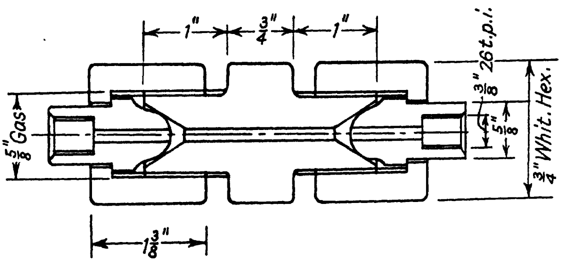


Fig. 118.—Pipe union, 750 atms. Steel.

For introducing electrical leads into high-pressure vessels the American Instrument Co. supply the design shown in Fig. 121.

The arrangement is clear from the drawing. This firm also supply a special type of magnetic regulator (Fig. 121) which permits of the operation of a system under a gas pressure less than the pressure of a connected high-pressure gas storage, and this fitting is also applicable to the by-pass line of a compressor between the discharge and intake when a constant delivery is desired. The valve consists of an electromagnet and a needle valve. The core, being magnetised by the closing of the circuit, pulls the valve from its seat, admitting gas from the pressure side. A break in the circuit causes the core to lose its magnetism, releasing the valve which is reseated by the valve spring. The operation of the valve may be controlled by the gauge, in which the circuit is completed between the Bourdon tube and adjustable contact points.

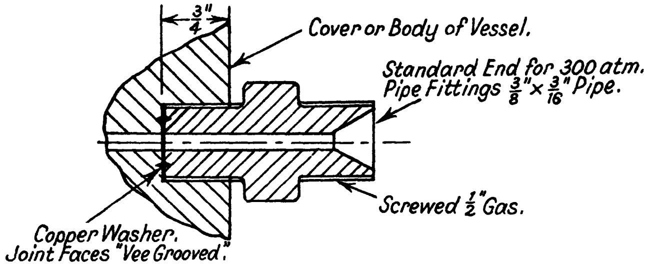

3/4"
Cover or Body of Vessel.
Standard End for 300 atm. Pipe Fittings 3/8"×3/16" Pipe.
Screwed 1/2" Gas.
Copper Washer. Joint Faces "Vee Grooved".

FIG. 119.—Nipple for attaching pipe lines to vessels.

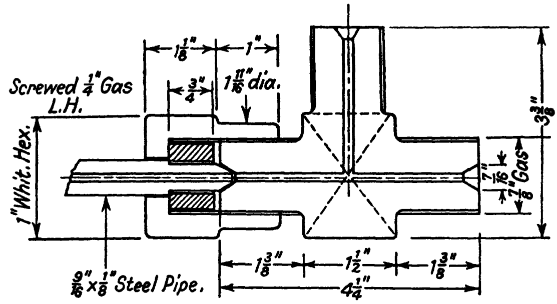


FIG. 120.—Tee-piece, 750-1250 atms.

Closure of High-pressure Vessels.

Self-Sealing H.P. Vessel Cover Joint.

A self-sealing type of new cover joint for both large and small reaction vessels has been recently patented by the Hochdruck Apparatebau of Dortmund, Germany (see Fig. 122).

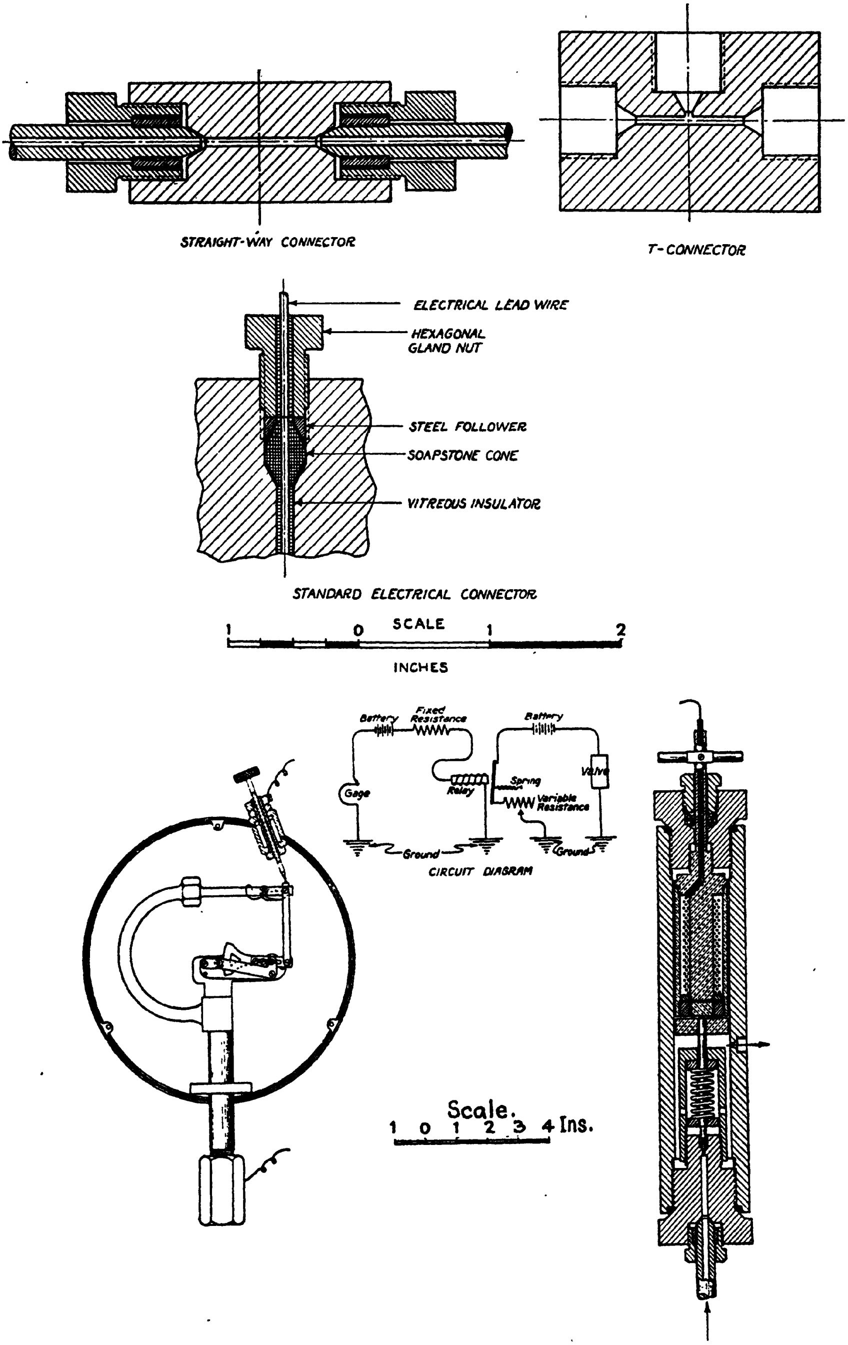


FIG. 121.—Pipe fittings for 1000 atms. and magnetic regulating valve for high pressures.
(American Instrument Co.)

By the pressure prevailing in the interior of the vessel, the cover plate *a* is pressed against a packing ring *b* of conical section. This packing ring, which is made of a material having a high modulus of elasticity, is thereby not stressed beyond the elastic limit, so that it does not take a permanent set nor show any deformation after dismantling. The axial component of the pressure on the packing ring is taken up by a split retaining ring *c*, which rests against a turned recess in the flange of the vessel. A ring nut, or an assembly ring *d*, serves for keeping the parts in their proper position ; they are under no load from the working pressure.

The principal advantages claimed for this construction over the bolted-on covers are the following : complete and permanent tightness, even under fluctuating working pressure ; convenient assembly and dismantling due to the absence of the large number of studs and nuts ; above all, a considerable reduction in cost, since the material otherwise used for the studs is very expensive, while the flange and the cover can be made of smaller dimensions owing to the absence of studs. As stated by the designers, a saving in cost of some 7000 marks can, for instance, be obtained over a bolted-on cover in the case of a high-pressure vessel of 1300 mm. (51 ins.) diameter of opening and a working pressure of 200 atms. (2800 lbs. per sq. in.).

It is stated that this new type of cover has been found to answer service requirements under various working conditions ; it has been tried in practice up to a diameter of 1 m. (3·3 ft.).

The " Vickers-Anderson " Type of Joint is of considerable interest in connection with large high-pressure chemical plant.

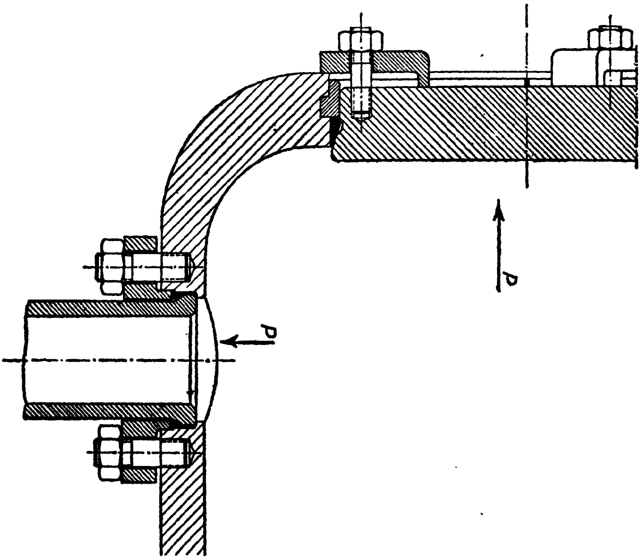
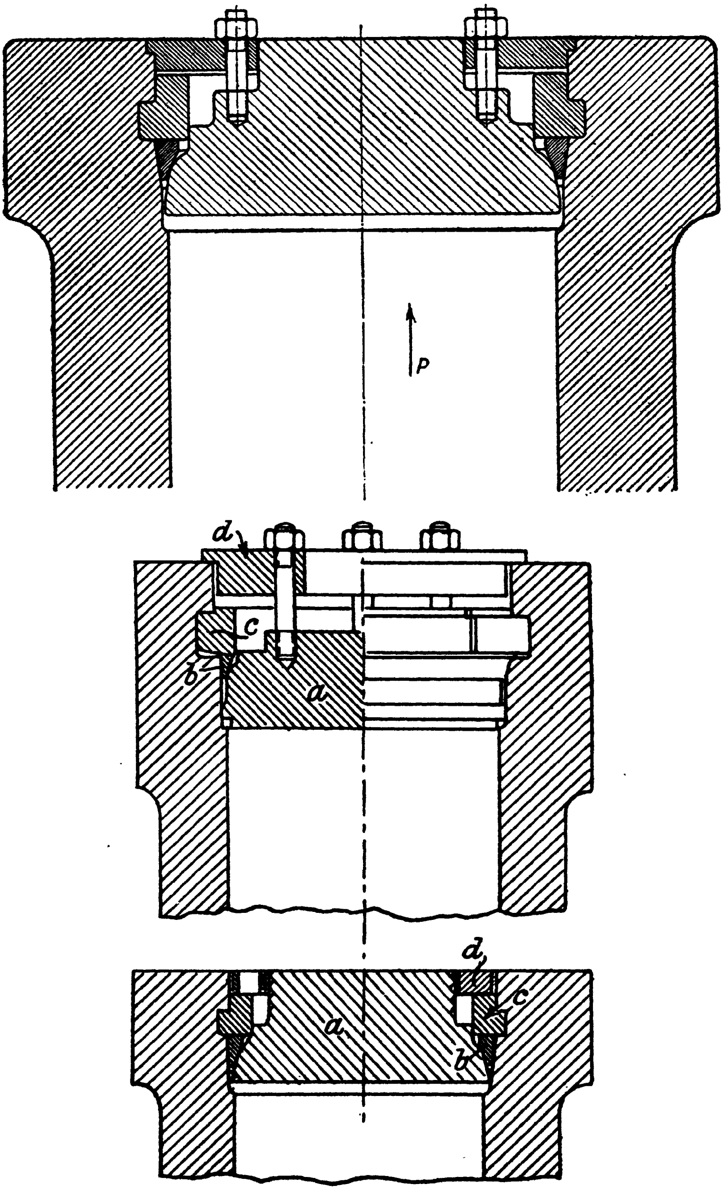
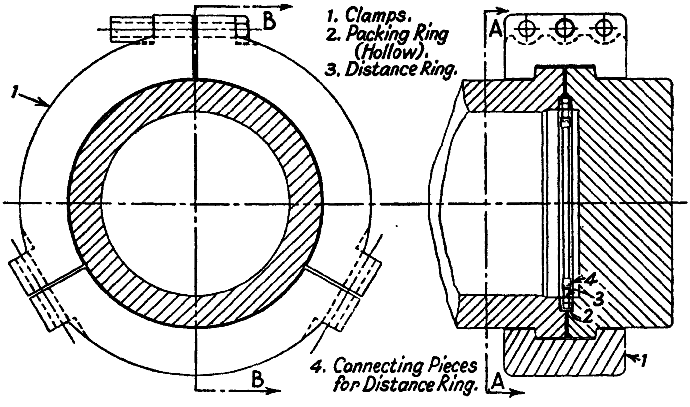


FIG. 122.—Hochdruck Apparatebau

The ordinary flanged and bolted joint is very commonly adopted for joints in pipes and vessels. For large diameter pipes and vessels subjected to high pressures this type of joint requires very heavy flanges, which are both cumbersome and costly. The joint known



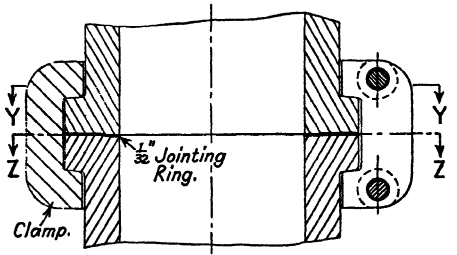
self-sealing cover joint.


1. Clamps.
2. Packing Ring (Hollow).
3. Distance Ring.
4. Connecting Pieces for Distance Ring.
B
B
A
A
1
1
2
3
4

Section thro' A.A. Section thro' B.B.

FIG. 123.—Vickers-Anderson joint.

as the Vickers-Anderson joint was introduced as an alternative to the flanged and bolted joint with the object of reducing the overall size of large joints.



Section at X.X.

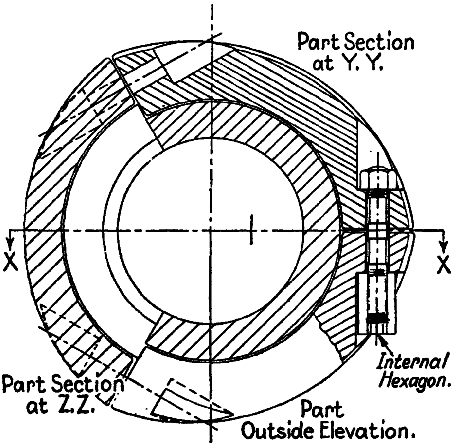


FIG. 124.—Vickers-Anderson joint.

The general features of this type of joint are illustrated in the accompanying drawings (Figs. 123, 124). A raised " shoulder " is machined on the two component parts of the joints with an inclined face which is made less than the angle of friction. The two parts are brought together so as to enclose some form of jointing ring, and a number of clamp ring segments (usually three or more are bolted together round the joint so as to pull it firmly together). The clamp ring segments are recessed and the sides of the recess are machined to the same angle as the faces on the raised shoulders. It will be appreciated that the joint calls for a very high standard of workmanship during manufacture with very fine working limits. In spite of this, it is finding favour as a means of making joints in large high-pressure vessels, and is also receiving consideration for joints in high pressure-high temperature steam plant.

The jointing ring may take the form either of the ordinary packing ring enclosed within a spigot, or a hollow steel ring, reinforced by an internal packing ring to resist collapse when tightened up. The internal packing ring is made of a number of separate pieces joined together, and there is provision—grooves or small holes—for free access of the fluid under pressure to the inside of the hollow ring. When the hollow ring is used, the joint is what is termed "self-tightening," that is, if the joint is tight against a small pressure, increase of pressure tends to tighten the joint further on account of the extreme flexibility of the hollow ring. On the other hand, with the ordinary packing ring the chance of leakage increases as the pressure increases, and the joint must be tightened up hard initially. Somewhat heavier clamps are therefore required when the ordinary packing ring is used to make the joint.

The accompanying drawings illustrate the joint with the two types of jointing ring referred to. Fig. 123 shows a joint suitable for a large diameter high-pressure vessel, whilst Fig. 124 shows the joint adapted to a high-pressure steam joint.

I am indebted to Imperial Chemical Industries Ltd. for the above information.

As an instance of the application of the Vickers-Anderson joint to vessels other than those used in chemical plant, mention may be made of the high-pressure wind tunnel at the National Physical Laboratory, which is used for aeronautical research. This tunnel is 17 ft. internal diameter, and is built up in sections jointed together by Vickers-Anderson joints.

Other types of cover joints for high-pressure vessels, most of which are applicable both to large and small openings, are shown in Figs. 125-133.

The first three (Figs. 125, 126, 127) are of the type in which the closure is made by screw threads. The first (Fig. 125) comprises a plug which is brought home against the joint ring by a right and left-hand screw coupling nut. The second (Fig. 126), gives details of two forms of plug closure with a cap nut, and the third (Fig. 127), again shows a method using a right- and left-hand thread coupling nut. Figs. 125 and 127 are not recommended except for low pressures.

The remainder (Figs. 128-133) are of the flanged pattern, with studs or bolts and nuts. The most frequently used are Fig. 128

and Fig. 129. Fig. 128 comprises a flanged cover-plate with a spigot guide fitting closely the bore of the vessel. The vessel mouth is coned, and the joint is made on quite a small area, as shown in the sketch. This type is extensively used in Germany. The lens ring type (Fig. 129) is used by Michels of Amsterdam and by Imperial Chemical Industries, and the construction is clear from the sketch.

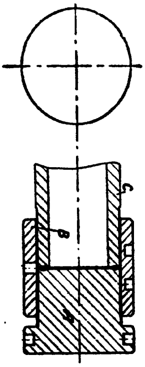


FIG. 125.

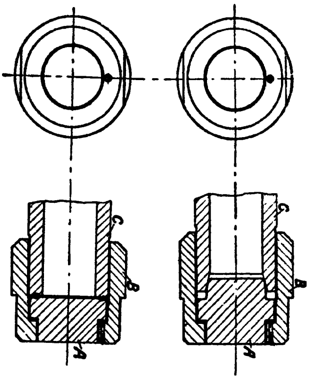


FIG. 126.

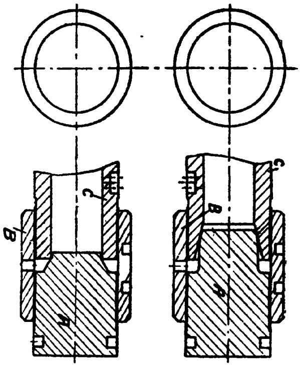


FIG. 127.

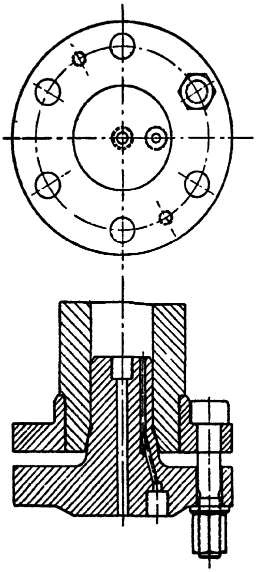


FIG. 128.

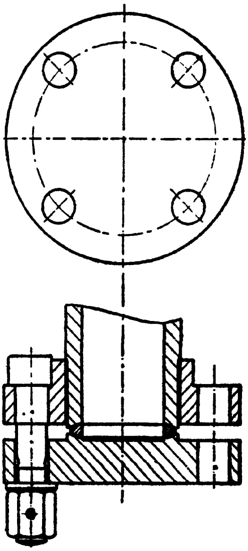


FIG. 129.

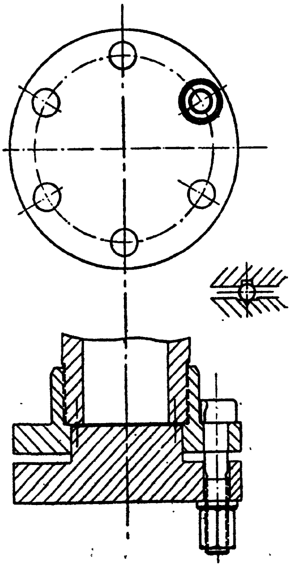


FIG. 130.

Fig. 131 shows a flanged cover with a spigot and recess type of joint. This is not recommended as it is very difficult to remove the joint ring without damaging the joint face on the body. Fig.

132 comprises a flanged joint wherein the joint is made on two knife edges, with a disc of soft iron or steel as the jointing material. This type was developed by Ipatieff. Fig. 133 shows a type of joint sometimes used for medium pressures, but it suffers from the same defect as Fig. 131.

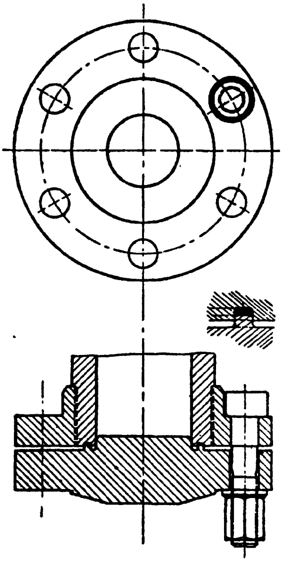


FIG. 131.

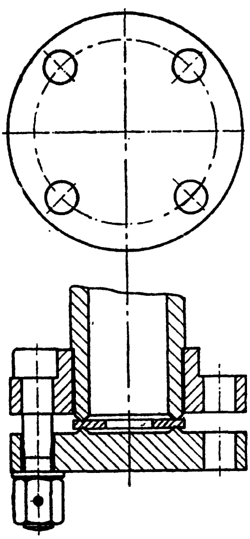


FIG. 132.

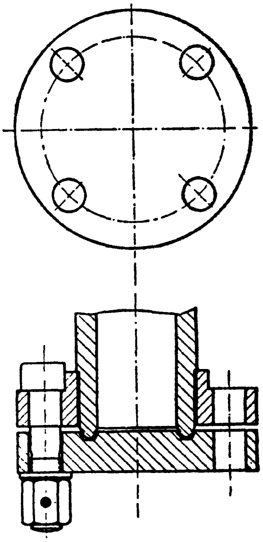


FIG. 133.

A type of jointing which I have developed at the Chemical Research Laboratory for all pressures as high as 3000 atms. is described in detail in Chapter VIII.

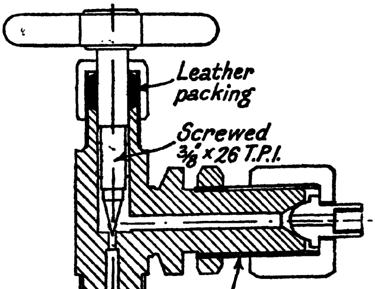


FIG. 134.—Bronze value for 300 atm. pressure.

Valves.

Wherever possible in high-pressure work it is advisable to use stainless steel valves. They are, of course, expensive, but the initial cost is more than offset by the long life and freedom from trouble due to corrosion. For clean gases, such as hydrogen, nitrogen, etc., it is possible to use bronze valves up to 300 atms. pressure, and Fig. 134 shows a suitable design for use with $\frac{3}{8}$-in. × $\frac{3}{16}$-in. pipe. Figs. 135, 136, 137 show two designs of valves in "Staybrite" steel, one for 300 atms.

and one for 750 atms. Both these valves are of the same general type, in which the seating is removable, both for cleaning and skimming up purposes. The valve end and the valve seating are two cones with about 5° difference of angle between them. Thus the valve seats on a small area at the bottom of the taper. The valve end is fitted with a piston extension, a little under $\frac{1}{8}$-in. diameter, and this acts as a check on the flow of gas through the valve. Before the valve is fully open, three or four complete turns of the handle are necessary.

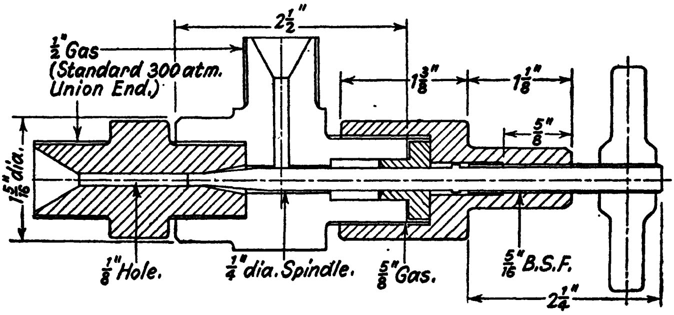


FIG. 135.—300 atm. valve.

The 300 atms. valve is fitted with $\frac{1}{2}$-in. gas, 60° coned ends for $\frac{3}{8}$-in. × $\frac{3}{16}$-in. pipe. If it is desired to screw the valve directly into the cover of the vessel, an end similar to Fig. 119 is arranged.

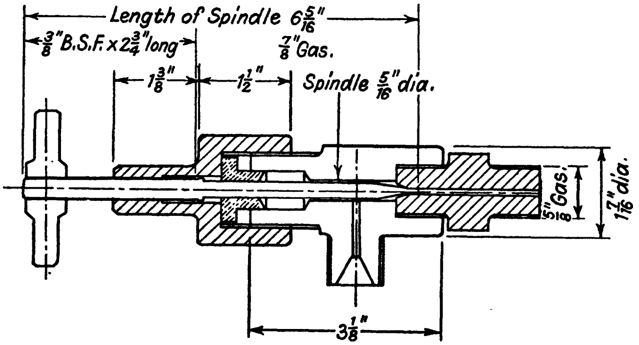


FIG. 136.—750 atm. valve.

Similarly, the 750 atm. valve gland side is adapted for $\frac{3}{8}$-in. × $\frac{1}{8}$-in. pipe connecting nipples, and the other side of the valve is shown as arranged for screwing directly into a cover-plate where a flat seating is necessary.

The gland packing for these valves is of tallow soaked leather rings. The gland is of phosphor bronze, and the gland nut may be of mild steel, since it does not come into contact with the gases flowing through the valve. The valve handles are made from ⅝-in. diameter round mild steel bar, and are pinned to the valve spindles, which are fitted with a stop collar, as shown, to prevent them being screwed too far out of the valve. For still higher pressure, Fig. 138 shows a valve in nickel-chromium-molybdenum steel for 3000 atms. on the point side of the valve, and a pressure not higher than 550 atms. on the gland side. Such valves are used for blow-off valves for 3000 atms. autoclaves, and outlet valves for appliances such as hand compressors, in which the pressure on the two sides of the valves varies by the amount given. It will be noted that this valve

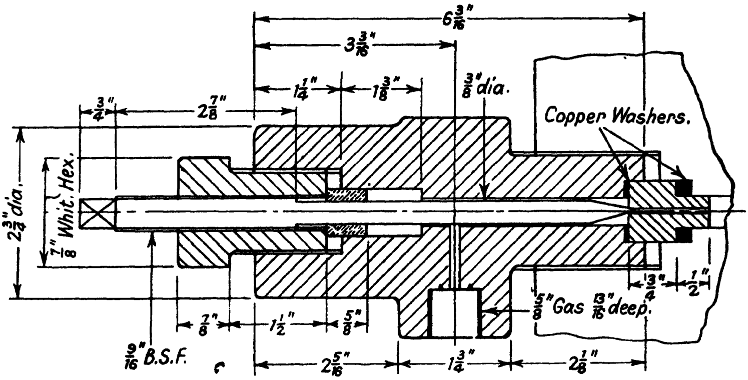


FIG. 138.—Stop valve, 3000 atms. on point side, 550 atm. on gland side.

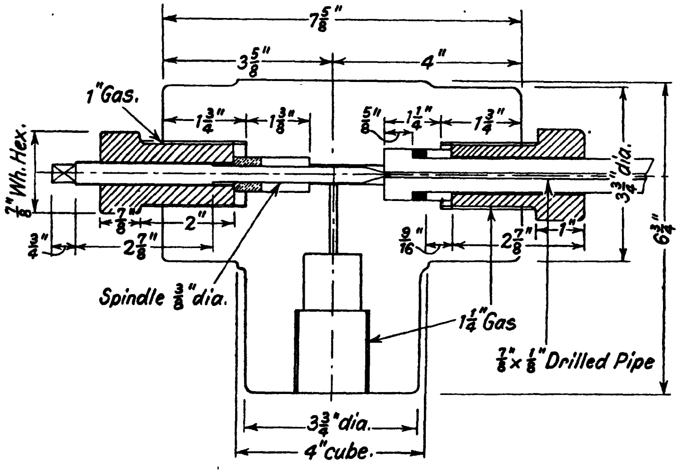


FIG. 139.—Valve for 3000 atm. pressure.

is fitted with a loose seating, which is easily renewed. At such pressure, particularly with hot gases, it is not possible to keep the valves absolutely tight for such long periods as in the case with work at 500-1000 atms., hence the facilities provided for skimming up the valve and seating. The packing for the gland is again of tallow soaked leather. Fig. 139 shows a valve for 3000 atms. on both the gland side and the point side. In so far as the pipe connection to the valve is concerned, it embodies Bridgman's unsupported area system in which the total pressure in the end of the pipe is transmitted to the much smaller area of the packing which is consequently subjected to greater pressure intensity and the joint is thereby " pressure sealed " in that within the limits of the material, the higher the pressure the tighter the packing.

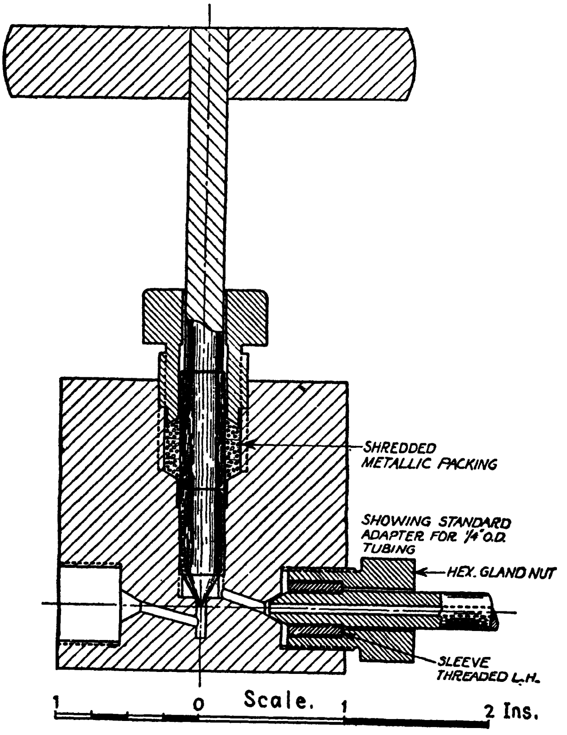

SHREDDED METALLIC PACKING
SHOWING STANDARD ADAPTER FOR 1/4" O.D. TUBING
HEX. GLAND NUT
SLEEVE THREADED L.H.
1
0
Scale.
1
2 Ins.

FIG. 140.—American Instrument Co.'s 1000 atm. valve.

The American Instrument Co. make a valve of the type shown in Fig. 140 for pressures up to 1000 atms. As in the case of the pipe line fittings made by this firm, and which have already been described, the pipe connection is made by coning the end of the pipe, and forcing this cone home against a cone of slightly smaller top diameter by means of a collar screwed on the pipe with a left-hand thread and a follower nut. The scale gives an idea of the dimensions of this valve.

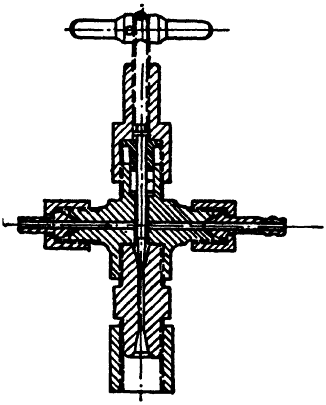


FIG. 141.—Fine adjustment valve with two or more outlets for gases or fluids.

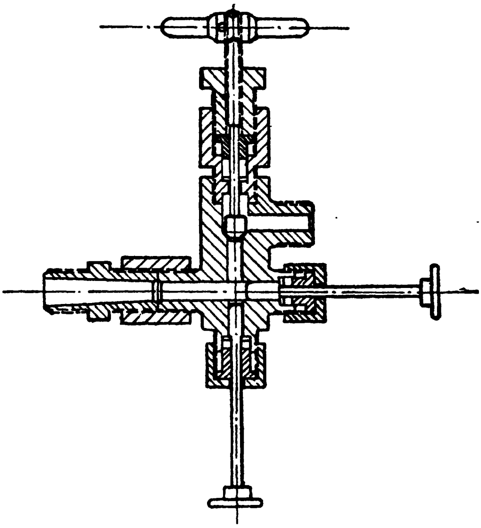


FIG. 142.—Ram valve for dirty or viscous fluids.

A series of different types of valves made by Andreas Hofer for pressures up to 1000 atms. are shown in Figs. 141-146. The titles beneath the valves describe these quite sufficiently. Pipe fittings standardised by Hofer for pressures up to 1000 atms. are

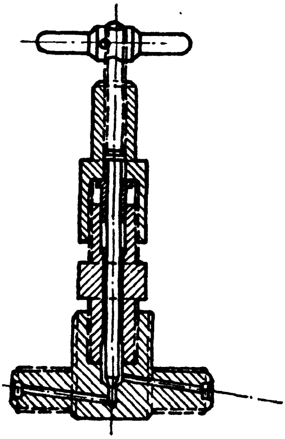


FIG. 143.—Fine adjustment straight through valve.

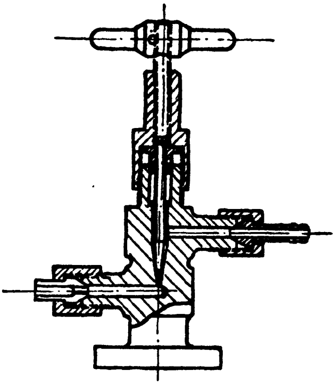


FIG. 144.—Fine adjustment valve with base flange.

shown in Figs. 147-152. All Hofer fittings up to 1000 atms. are screwed ½-in. gas thread.

A small high-pressure valve, as patented by Imperial Chemical Industries and made by Hopkinson of Huddersfield, is seen in Fig. 153.

This type of valve has been used successfully, in small sizes up to ⅝-in. bore, for pressures up to 800 atms., for both gases and liquids.

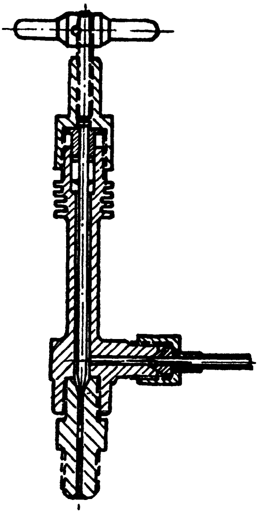


FIG. 145.—Valve for hot gases.

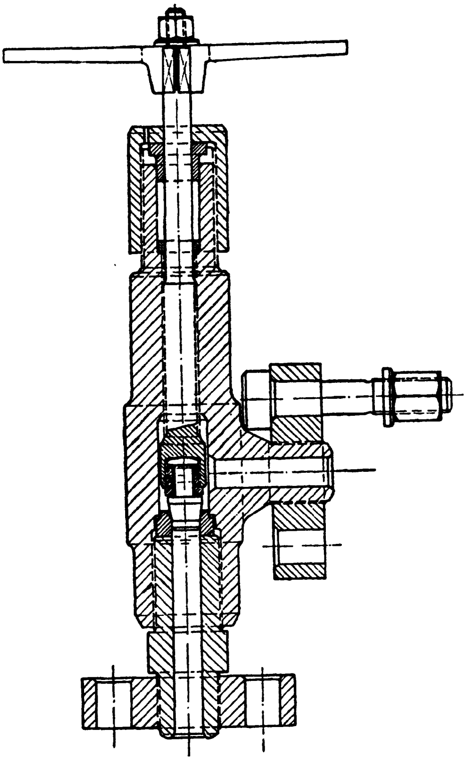


FIG. 146.—Fine adjustment valve with movable inset spindle.

The body is made in two parts, the joint being made by means of a lens ring, which also forms the valve seat. The valve nose is of the self-centring type. The bottom half of the body is made in two types to give either a right angle or a straight-through valve.

A large high-pressure oil operated valve, also patented by Imperial Chemical Industries and made by Hopkinson, is seen in Fig. 154.

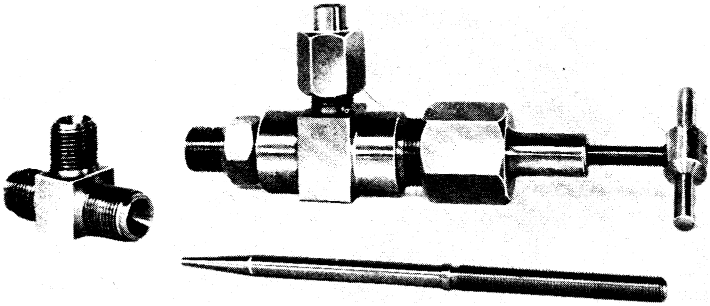


FIG. 137.—Photograph of 300 atm. valve in stainless steel, with spare spindle and tee-piece.

[*See page* 207.

[*To face page* 212.

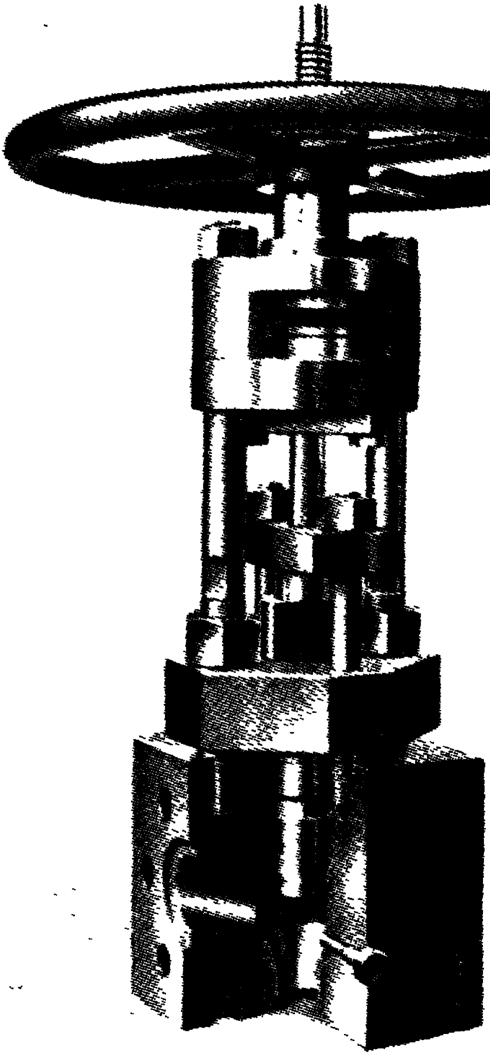


FIG. 155.—High-pressure valve. (Hochdruck Apparatebau.)

[*To face page* 213.

Hydraulic operation has been adopted as a means of giving a quick acting remote control of the larger sizes of valves.

The illustration shows a 3-in. bore right angle valve, of a type in normal use for gas and liquids at 250 atms. The operating cylinder is combined with the valve body, and is single acting, the valve being closed by oil pressure, and opened by the pressure of the system when the oil is released. As a safeguard against accidental opening, as a result of failure of the oil supply, or faulty operation, hand-operated locking gear is fitted, which can be screwed down to hold the plunger whenever the valve is closed. The oil pressure used in this valve is 350 atms.

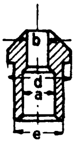


FIG. 147.

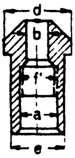


FIG. 148.

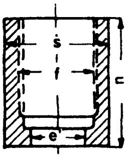


FIG. 149.

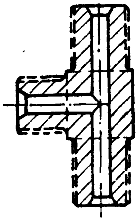


FIG. 150.

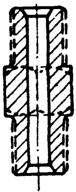


FIG. 151.

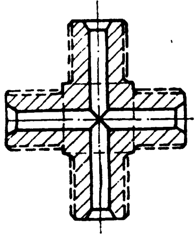


FIG. 152.

FIG. 147.—Pipe nipple with plain bore.

FIG. 148.—Pipe nipple with screwed bore.

FIG. 149.—Union nut.

FIG. 150.—Tee-piece.

FIG. 151.—Pipe union body.

FIG. 152.—Cross-piece.

Hofer pipe fittings.

The Hochdruck Apparatebau also manufacture a series of patented high-pressure stop valves. It is the opinion of this firm that the best way of ensuring tightness is to press two cones of different angles together in such a way that the tightening is produced by means of line contact. In this way tightness is ensured with the application of a minimum amount of force.

Fig. 155 shows one of such valves partially sectioned. The actual valve is of elastic material inserted loosely between the

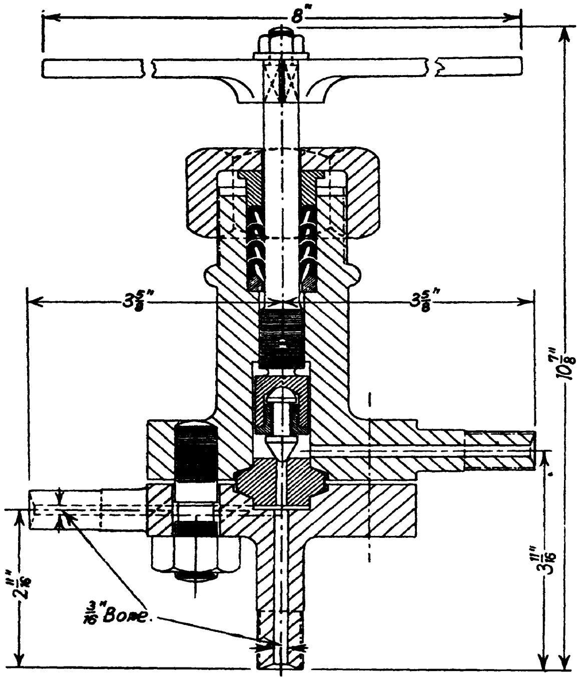


Fig. 153.—Small high-pressure valve for 300 atm. pressure. (Imperial Chemical Industries.)

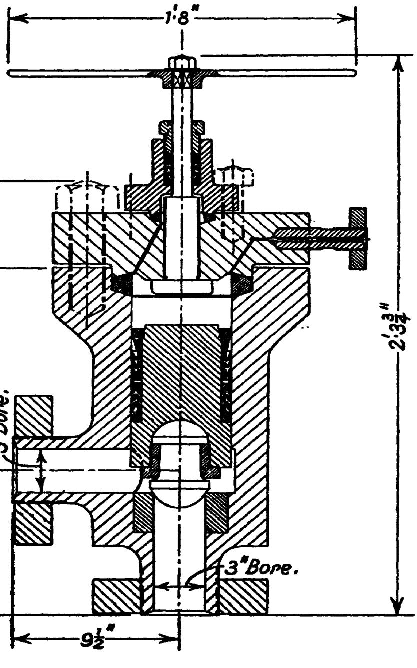


Fig. 154.—Large high-pressure oil operated valve. (Imperial Chemical Industries.

spindle and seating. The spindle has a linear motion, and the handwheel nut thrust is taken on a ball-bearing. When the valve is fully open, the stuffing-box packing is shielded from the material flowing through the valve by a cone seating on the rising spindle. Water-cooled glands can be arranged if desired.

The pattern shown is for working pressures of 150 atms.

High-pressure Reducing Valve.

The satisfactory utilisation of solid carbon dioxide for various purposes has introduced new problems which have had to be solved according to the particular application, as, for example, the process of liquefying the solid carbon dioxide and subsequently passing it in the gaseous state to bottling machines. The "Penguin" reducing valve has been developed with a view to maintaining automatically a substantially constant supply of gas over a wide range of pressures. Although it has been designed primarily for use in conjunction with the "Drikold" (solid carbon dioxide) liquefier it may also be utilised with any container where it is desired to maintain a constant exit pressure from a gas supply at a higher pressure. The diagram

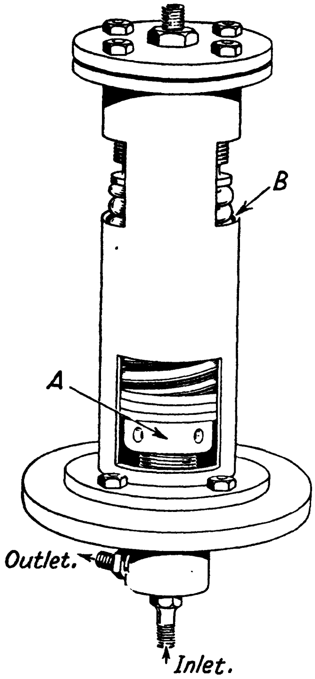


FIG. 156.—"Penguin" high-pressure gas reducing valve.

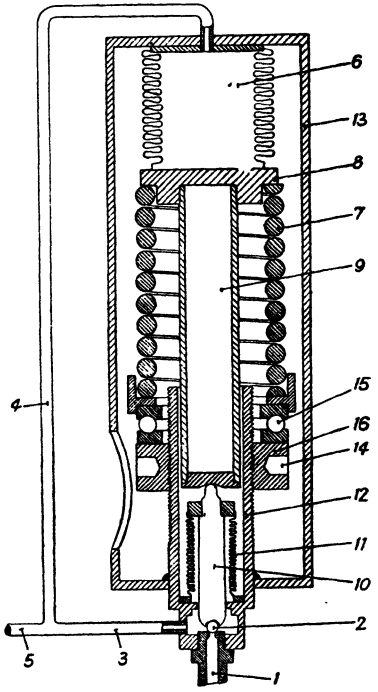


FIG. 157.—Section of "Penguin" high-pressure gas reducing valve.

(Figs. 156, 157) illustrates the general appearance of the device. The required low pressure is obtained by adjusting the collar (A) at the base of the valve, which has the effect of altering the force exerted by the spring (B). The pressure thus determined will be maintained within very narrow limits during the withdrawal of the whole charge from the liquefier.

In the manufacture of mineral waters, the machine which carbonates and bottles the beverages is designed to work at a constant relatively low pressure, usually between 60 and 150 lbs. per sq. in., whilst the source of carbon dioxide for carbonation is generally obtained at an initial pressure of from 1000 to 1800 lbs. per sq. in., which pressure, of course, falls during the process.

Many reducing valves do not provide a constant low pressure with a falling pressure on the high-pressure side and with a fluctuating gas flow through the valve, and moreover usually embody glands or stuffing boxes which are a source of leakage. Because of the extreme wire drawing which occurs across the valve seat, there is a tendency for the valve to freeze up so that some form of heating is usually required. This is quite unnecessary with the " Penguin " valve which does not freeze up, even under the most exacting conditions.

The principle of the valve is shown in Fig. 157. The gas at high pressure is admitted to the underside of the ball valve 2, across which the pressure is reduced. Gas at low pressure is admitted into the bellows chamber 11, the upper diaphragm of which is free to move, and is connected to the valve spindle 10, so that any variation in gas pressure in this chamber tends to cause a corresponding variation in the load on the valve. It will be noticed that both the high pressure in the pipe 1, and the low pressure on the diaphragm referred to, both tend to cause the valve to lift off its seat.

The gas at low pressure is also admitted into a large diameter flexible bellows 6. In the diagram (which is merely schematic) this is done via the external connecting pipe 4, which is taken as a branch off the main low-pressure outlet. The upper end of the bellows 6 is fixed to the valve casing, but the lower end is closed by a movable diaphragm 8, the area of which is considerably greater than that of the movable diaphragm on the small bellows 11. Further, the pressure on the diaphragm 8 tends to force the valve on to its seat, the movement being transmitted by means of the central guided tube 9. A stiff spring presses on the under side of the diaphragm 8 and enables the valve to be set at any desired opening pressure.

It will be seen that any fall in the high pressure will cause a change in the gas rate past the valve, and therefore a fall of pressure in the bellows 11 and 6, as well as reduce the direct upward pressure on the valve arising from the high pressure itself. If the diaphragm 8 is very much larger than that of the small bellows and seat valve, the fall in pressure will reduce the downward load (tending to close the valve) much more than the upward load; consequently, the spring 7 which provides a constant large upward load will cause the ball valve to open further and allow the gas rate to increase until the forces on the diaphragm 9 are again in equilibrium. A similar result is obtained if the amount of low-pressure gas taken at the outlet of the valve should suddenly increase.

The information regarding this valve has been kindly supplied by Imperial Chemical Industries Ltd.

In concluding this chapter, it is perhaps advisable to repeat that the discussion of *materials* for pipe lines, valves, etc., in this chapter has been confined to operation at or about room temperature. Where the operating conditions include elevated temperature, care must be taken to select materials suitable for these conditions. As will be seen in the next chapter (which is devoted to the study of the properties of materials at elevated temperature), a number of special alloys have recently been developed for high temperature service, many of which are suitable for manufacture into piping and other fittings.

CHAPTER VII.

PART I.

MATERIALS FOR SERVICE IN HIGH-PRESSURE PLANT WHEN EXPOSED TO HIGH TEMPERATURE.

FOR work at ordinary or moderate temperatures it is quite satisfactory to design pressure vessels upon the basis of the mechanical properties of selected suitable materials, as revealed by mechanical tests (tensile-impact, etc.) carried out at room temperature. For example, the ordinary commercial gas cylinder, as described in a previous chapter, is designed on this principle ; the low-pressure steam boiler, air receiver, bleaching kier, steam-jacketed pan, etc., are other examples, and specifications by Lloyds, the insurance companies and other governing authorities include such tests to ensure soundness of material and suitability for the proposed duty. We have become accustomed to regard structural materials under such conditions as permanent both in properties and dimensions, and apart from troubles due to such factors as corrosion, the structurally useful life of the vessel or its component parts appeared to be quite independent of time.

With the advent of the high-pressure steam boiler and high pressure-high temperature chemical plant, attention was quickly drawn to the unsuitability of mechanical tests at ordinary temperature as a guide to the best materials or to the permissible working stresses in such circumstances.

It has, of course, been known for a long time that metals begin to lose their strength when exposed to even moderately high temperatures. The earliest recorded instance I can find of recognition of this fact in connection with steam plant is contained in the discussion on Perkin's well-known paper on his high-pressure steam plant which operated at pressures of 500 lbs. per sq. in. (*Proc. Inst. Mech. Eng.*, 1877, 133).

In the course of the remarks by Mr. D. Adamson of Hyde, the well-known boilermaker, criticising the employment of such high pressures, appears the following :—

" There was hardly an iron in the country that was not subject to a great reduction of strength when exposed to temperatures ranging from 500-700° (F.), and at such heats it was easily destroyed by percussive force, not even excepting Low Moor iron or mild steel, now justly so popular."

One of the first publications dealing exclusively with the behaviour of metals under stress at high temperatures is that of Dickenson (*Journ. Iron and Steel Inst.*, 1922, **106**, 103). The results of many tests he carried out showed that metals begin to lose their strength at temperatures higher than 300° C., and that the resistance to fracture when subjected to prolonged loads at high temperatures is less than when such specimens are quickly pulled at the same temperature. It was also soon discovered that tensile test specimens, when loaded for long periods at high temperatures, exhibit a phenomenon of continuous elongation or plastic flow, which is now generally known as " creep." This creep may continue for months at a slowly decreasing rate, as will be seen from the curve, Fig. 158 (*Proc. Inst. Mech. Eng.*, 1932, **122**, 209), which gives the creep history of a nickel-chrome-molybdenum steel stressed at 5 tons per sq. in. at a temperature of 450° C. Such " creep " tests of either long or short duration (coupled with ordinary tensile and impact tests at room temperature to prove quality of material) are now recognised as a useful basis for designs involving stress at high temperatures.

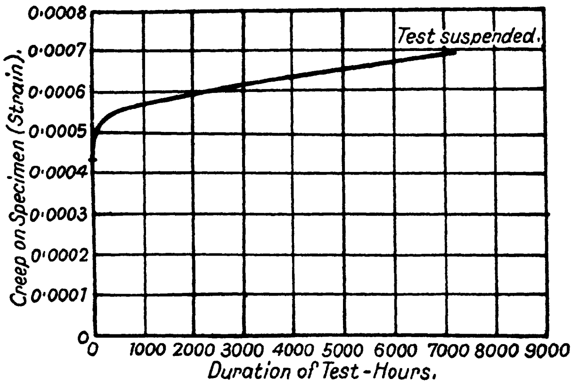


FIG. 158.

Investigations of creep are carried out by loading tensile test specimens to give various stresses at desired temperatures, and the elongation of the gauge length per unit time is measured as accurately as possible. It will be realised that a period of months is necessary to obtain reliable creep data for a given steel, and although short-time tests have been proposed and adopted by several workers, this practice has been criticised on the ground that the creep properties of some metals may alter considerably with time, due to slow structural change under stress at the temperature of test. There is also considerable difference of opinion in the case of workers using the same type of test in the evaluation of data so obtained in its application to actual practical problems.

Before entering into a more detailed discussion of these points, there are several aspects of creep upon which there appears to be general agreement, and which will now be dealt with.

Firstly, up to temperatures of 350° C. or so, the properties of ordinary mild carbon steel are in general similar to those at ordinary temperature, and it behaves as an elastic body, though with a stress range which diminishes as the temperature rises above 300° C. At temperatures higher than 350° C. the elastic range of such steels diminishes rapidly, until at 500° C. the elastic range is so small as to be negligible, the steel becomes plastic, and therefore liable to continuous deformation under stress. Heat-resisting steels, and steels developed for high temperature service, are of course less liable to continuous deformation or plastic flow under stress at elevated temperatures, but even these steels are by no means without "creep" under working conditions, small though this may be.

Hence we must accept this idea of continuous "creep" of stressed parts of high-temperature high-pressure plant, and the important point very often is the value the designer is prepared to accept as a permissible deformation per unit time.

For example, Baumann (*Proc. Inst. Mech. Eng.*, 1930, 1039) discusses this point at some length, and suggests the following

TABLE 2.

Material.	Temperature °C.	Limiting Creep Stress based on Creep Rate of 10^{-5} in./in./day. Tons/sq. in.	Ult. Stress Short-time Tensile Test. Tons/sq. in.
0·5 per cent. carbon steel	300	30·0	48·0
High chromium steel .	300	31·5	42·0
Nickel chrome steel .	300	30·3	49·0
0·5 per cent. carbon steel	400	16·0	37·0
1·7 per cent. manganese steel	400	15·5	36·5
0·5 per cent. carbon cast steel	400	12·0	34·0
High chromium steel .	400	19·5	38·0
Nickel chrome steel .	400	7·6	38·0
High chromium steel .	500	4·5	30·6
Nickel chrome steel .	500	1·5	27·3
Chrome vanadium steel .	500	1·9	41·5

permissible creep for various parts of a steam power plant where creep conditions apply :—

	Strain.
(1) Turbine discs pressed on shafts	10^{-9} per hour.
(2) Bolted flanges turbine cylinders . . .	10^{-8} ,,
(3) Steam piping—welded joint—boiler tubes .	10^{-7} ,,
(4) Superheater tubes	10^{-6} ,,

The second point upon which authorities are in general agreement is that the rate of creep appears to be independent of the short-time tensile properties at the same temperature. This is illustrated very clearly in the table on opposite page (taken from Tapsell's book, " The Creep of Metals," Oxford University Press, 1931, by permission of the author and publishers).

It will be seen that the difference between the strength given by the short-time tensile test and the limiting creep stress increases rapidly as the temperature rises, until at 500° C. the difference is really remarkable.

Thirdly, the heat-treatment of the steel prior to creep tests has a considerable influence upon the rate of creep.

TABLE 3.

Comparison Between the Creep Rate of Normalised and Hardened Carbon Steel. (Kanter and Spring.)

Material, 0·35 Per Cent. Carbon Steel.

Condition.	Temp. of Test °C.	Short-time Tensile Test. Ult. Strength. Tons/sq. in.	Creep Tests.	
			Stress Applied. Tons/sq. in.	Rate of Creep, in./in./day.
Normalised . .	425	30·0	4·47	0·00000408
Quenched 845° C. Tempered 540° C. .	425	31·4	4·47	0·00000504
Normalised . .	540	20·4	1·34	0·00000580
Quenched 845° C. Tempered 540° C. .	540	19·4	1·34	0·0000190

As a result of long experience with high temperature-high pressure plant, Imperial Chemical Industries Ltd. have come to the following conclusions in regard to creep. (Private communication from the Company, to whom I am greatly indebted for permission to publish it.)

Within the creep region, if a metal is subjected to a steady load at a given temperature and strain measurements are taken at intervals, a curve similar to Fig. 159 is obtained.

This curve can usually be considered as consisting of the following stages :—

1. The metal elongates rapidly during the first few hours after the application of the maximum stress.
2. This initial flow is followed, if the applied stress is not too great, by a period in which the rate of creep is much less than in the first period, and decreases uniformly, and, either the rate of strain becomes constant, or
3. There is a sharp increase in the rate of creep and fracture will then take place.

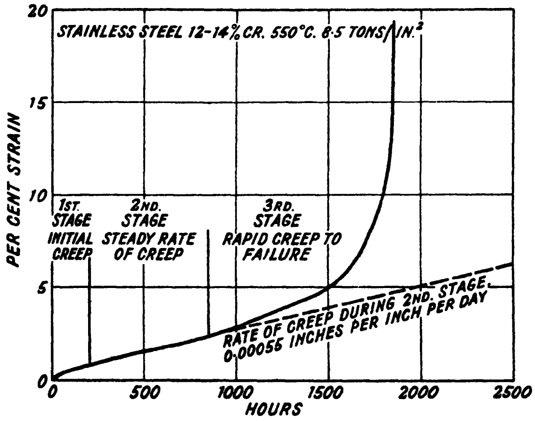


FIG. 159.

Naturally, the working stress for any design must be such that stage 3 does not arise in the time-strain curve for that stress. The working stress should be such that the steady rate of creep attained in stage 2 (above) will not give rise to excessive deformation during the expected life of the part concerned. From a series of curves of the type shown in Fig. 159, the stress-rate of creep curve shown in Fig. 160 can be drawn, and from such a curve the designer can determine the working stress which will not cause excessive deformation. As already stated, the term " excessive deformation " may vary according to the nature of the design.

The general conclusions arising from published creep data and long practical experience in the Company's plants may be briefly summarised as follows :—

1. The load carrying ability of all the " pearlite class " of steels at temperatures of 600° C. and above is practically nil. This class includes all the generally used engineering steels—chrome-vanadium, nickel-chrome, mild steel, etc. Where good strength at temperatures of 600° C., and above, is required, an austenitic steel must be used.
2. For each steel there is a temperature at which the creep strength falls off very rapidly. When such a temperature is reached, an increase in temperature of less than 50° C. may result in a reduction in creep strength of over 80 per cent. The necessity for very careful temperature measurement and control on plants operating at elevated temperatures must therefore be appreciated.

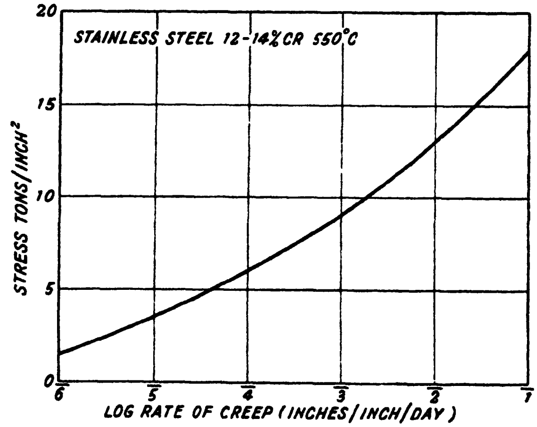


FIG. 160.

3. The presence of nickel in a pearlite steel does not seem to confer any benefit as regards creep strength in the range 400-600°.
4. The addition of certain small percentages of molybdenum greatly increases the creep strength in the range 400-600° C. Thus the addition of about 0·35 per cent. of molybdenum to an ordinary mild steel improves the creep strength in the range 450-550° C. by about 100 per cent.
5. The addition of chromium to pearlite steels up to about 1 per cent. greatly improves the creep strength up to 500° C. The further addition up to about 6 per cent. gives only a slight additional improvement, whilst increases beyond 6 per cent. give practically no further improvement.

6. It is important to note that the physical condition of a steel after very long periods, under working conditions involving stress and elevated temperatures, may change. In time a steel may develop different creep characteristics to those it originally possessed. Thus, it has been shown that a 0·4 per cent. carbon steel, after 2000 hours at 560° C., may have a rate of creep at 500° C. ten times as great as the rate of creep under the same stress at 500° C. before the steel had been given the above treatment.

A paper was recently given before the American Institute of Chemical Engineers by J. L. Cox, Chief Engineer of the Midvale Steel Company, in which the author dealt at length, firstly, with the properties of structural materials at high temperature, and, secondly, with the attack of steels by hydrogen and hydrogen-nitrogen mixtures at high temperature and pressure.

I am indebted to the author and to the American Institute of Chemical Engineers for permission to include the following extensive abstract of the paper (which was taken from a corrected proof).

After introducing the paper by a description of the methods used in obtaining creep data, and of the peculiarities of "creep," Cox discusses the effect of composition upon the properties of materials at high temperature, and states :—

Chemical composition is of as much importance in resisting stress at super-atmospheric temperatures as at lower temperatures. Within the strain-hardening range carbon is considered to increase resistance to strain up to about 0·4 per cent., with but little gain above that figure on long time tests, which is very different from its hardening power in short tests. Being readily oxidisable, carbon steels are unfit for use much over about 480° C. If used, due allowance must be made for loss of section by scaling.

Experience shows, and Chevenard's experiments prove ("The Mechanical Properties of Metals at Elevated Temperatures. Symposium on Effect of Temperature on Properties of Metals," *Am. Soc. Mech. Engrs. and Am. Soc. Testing Materials* (1931), pp. 245-268), that an alloy more nearly approaches a rigid body than does a pure metal, and preserves this property at a higher temperature ; also that, generally speaking, small additions of strengthening elements are more effective, proportionately, than large additions, and that small additions of several elements are more effective than an equal addition of a single element.

Among the lower alloys for use at moderate temperatures, one of much promise is a low carbon-manganese-chrome-molybdenum steel, which at 480° C. shows in 700 hours at a stress of 20,000 lbs. per sq. in. no extension as great as one fifty-thousandth of an inch.

At 25,000 lbs. per sq. in. it has a creep rate of about 0·2 per cent. in 1000 hours. The composition of this steel is C 0·25 per cent., Mn 0·95 per cent., Si 0·20 per cent., Cr 0·62 per cent., Mo 0·20 per cent.

Nickel alone, in moderate proportions, has little effect on the creep values of steel. Tapsell and Johnson and Clenshaw ("Properties of Materials at High Temperatures: No 6—The Strength at High Temperatures of Six Steels and Three Non-ferrous Metals," *Dept. Sci. Ind. Res. (Brit.), Sp. Rep.*, No. 18 (1932)), found a 3·43 per cent. nickel steel no better than plain 0·50 carbon steel at 400° C., and above. The addition of 0·24 per cent. chromium did not improve it nor was C 0·35, Mn 0·66, Cr 1·18, V 0·25 per cent. equal to the nickel and carbon steels at 500° C. Bailey, Dickenson and others ("The Trend of Progress in Great Britain on the Engineering Use of Metals at Elevated Temperatures. Symposium on Effect of Temperature on Properties of Metals," *Am. Soc. Mech. Engrs. and Am. Soc. Testing Materials* (1931), pp. 218-236) found 3-3½ per cent. nickel with about 1 per cent. chromium little, if any, superior to a good mild steel at temperatures between 400 and 500° C., and doubted if nickel was of any advantage in improving the load-carrying ability of this type of steel at elevated temperatures.

Chromium is very active in raising creep strength. It is the basis of most heat-resisting alloys, increasing strength and decreasing oxidation. At about 5 per cent., combined with one-half per cent. of molybdenum in a low carbon steel, it has over twice the creep strength of carbon steel at 540° C., and offers fair resistance to oxidation and corrosion. Stainless iron, carrying about 0·10 per cent. carbon and 15 per cent. chromium, has somewhat over twice the creep strength of a plain 0·11 per cent. carbon steel from 400 to 500° C., and fair strength above that range, besides a good degree of resistance to oxidation, but it has a high initial elongation.

The straight chromium steels with high chromium possess greater creep strength and greater resistance to oxidation, but have very low impact strength and are liable to great coarsening of the grain on long exposure to heat. A small addition of nickel helps greatly to restrain this growth.

Combined with nickel in varying proportions, chromium produces the best commercial refractory ferrous alloys available in quantity to-day. They can be further strengthened by small additions of molybdenum, tungsten, titanium, etc. The well-known alloy "18 and 8," having from 18 to 20 per cent. chromium and 8 to 10 per cent. nickel, has excellent creep properties. It belongs to the class of austenitic alloys, having a face-centred cubic lattice, whereas ordinary steels are body-centred. Although the austenitic alloys are comparatively soft at atmospheric temperature, they are much more slowly softened by heat than is the other type, and are far stronger at high temperatures. For use at medium high temperatures the 18 : 8 alloys should have a very low carbon, and should not be given the usual high quench if it is to be used in the range of about 510-700° C., in which it may otherwise become embrittled and suffer intergranular weakening. At higher temperatures the carbides precipitated in this dangerous temperature range, which are the cause of the trouble, are in solid solution, permitting the use of higher carbon and a cheaper raw material. Titanium in small amounts is reported largely to correct this intergranular weakening.

For severe conditions even higher ferrous alloys are used :—

PERCENTAGE OF ALLOYING ELEMENTS.

Cr.	Ni.	W.
25	10	—
25	20	—
30	30	—
20	35	—
20	8	4
12	60	2·5

All these are well-known compositions. The last two are Hadfield's HR-1 and Commentry-Fourchambault and Decazeville's BTG metal, the latter being the alloy used for catalyst bombs in the Claude process for synthetic ammonia, operating at a temperature of about 565° C., and at a pressure of about 1000 atms.

Apart from creep, there is the important feature of structural stability to consider in connection with the use of materials at high temperatures. For example, Bailey and Roberts (*Proc. Inst. Mech. Eng.*, 1932, **122**, 209) found that in the case of carbon steels there is a general tendency for spheroidisation of the cementite when these steels are subjected to long exposures over 400° C. They examined a superheater tube (0·16 per cent. carbon steel) and found that although it appeared to remain structurally stable at 300° C., portions which had been at temperatures of 400-475° C. showed that the original lamellar pearlite had become completely spheroidised. They also found that an annealed tube required a temperature of at least 50° C. higher than an unannealed tube, which had been strain-hardened in manufacture, for spheroidisation to occur in the same time. Another interesting result was that a 0·9 per cent. carbon steel showed a reduction of 25 per cent. in the stress required to produce a given creep rate when the steel was fully spheroidised than when the cementite was in the lamellar condition. Since the resistance to creep is less in the spheroidised condition and annealing appears to retard this structural change, Bailey and Roberts suggest that for high temperature service, carbon steel for superheater and main steam pipes should be fully annealed after working.

Bailey and Roberts also noted considerable embrittlement of several types of steel when stressed at high temperatures, and table on the next page shows the results of tests made to investigate this important factor.

A great deal of experimental work on the subject of embrittlement has been carried out in the research department of the Imperial Chemical Industries Ltd., Billingham, during the past three or four years. Table 5 represents the results obtained, and it will be seen that nineteen different steels have been examined after a period under various stresses and temperatures in the range 350-450° C. The method of testing was to subject the specimen to a definite stress and temperature for eight hours, and then allow it to cool during a further period of eight hours, whilst still under stress. This cycle was repeated fifty times, and impact tests were then made. In general, the results presented in Table 5 and those presented by Bailey and Roberts are in very striking agreement, save that some evidence was present in the Billingham work (not entirely conclusive) that the stress imposed during the period of heating did influence the degree of embrittlement produced. For example, a nickel-chromium-molybdenum steel (note: low molybdenum, viz. 0·24 per cent.) after fifty cycles at 10 tons per sq. in. and 450° C., suffered a reduction in impact value of 73-86 per cent., whereas the same steel, after fifty precisely similar cycles, save that no stress was applied, suffered a reduction in impact value of 40-47 per cent.

It is to be noted that there are two distinct types of embrittlement of steels and alloys when these are maintained under stress for some time at high temperatures. The first type is of the nature of "temper brittleness," and engineers who have used nickel-chrome steels will know that these steels are particularly liable to this very serious embrittlement when held at temperatures of 400-550° C. This "temper brittleness," as will be seen from the tables, is not confined to nickel-chrome steels, and it is noteworthy that such embrittlement is not accompanied by any marked change in the test results obtained from the tensile test. A notched bar form of impact test, such as the Izod, is the only method by which it may be detected.

TABLE 4.

EMBRITTLEMENT OF STEELS UNDER STRESS AND ELEVATED TEMPERATURES.

No.	Composition of Steel. Per Cent.						Heat Treatment °C. O.H. = Oil Hardened. T. = Tempered.	Brinell Hardness.	Embrittling Treatment.			Impact. Ft.-lb.		Reduction Impact Value. Per Cent.
	C.	Mn.	Ni.	Cr.	Mo.	Cu.			Stress. Tons/sq. in.	Temp. °C	Time. Hours.	Initial Condition.	After Treatment.	
1	0·34	1·08	1·44	0·18	nil.	—	O.H. : 850, T. : 650	255	0	450	200	45, 48	6, 9	84
							O.H. : 850, T. : 650	255	10	450	250	45, 48	7, 13	79
2	0·28	0·65	3·38	0·6	,,	—	O.H. : 830, T. : 650	270	0·5	450	100	54, 56	7, 9	86
							O.H. : 830, T. : 650	270	10	450	100	54, 56	3, 4	93
3	0·34	0·64	3·34	0·72	0·21	—	O.H. : 843, T. : 593	290	5	450	250	44	19	57
4	0·30	0·63	3·27	1·05	0·4	—	O.H. : 850, T. : 650	290	5	450	100	32, 34	24, 29	20
5	0·21	0·56	3·1	1·25	0·56	—	O.H. : 850, T. : 650	287	5	450	200	71, 73	39, 46	41
6	0·26	0·59	3·14	1·07	0·57	—	Unknown.	306	5	450	200	51, 53	20, 20	62
7	0·30	0·45	2·51	0·81	0·57	—	Unknown.	257	5	450	200	33, 35	26, 31	16
8	0·30	0·53	2·37	0·62	0·65	—	O.H. : 830, T. : 650	285	0·5	450	100	38, 45	43, 43	nil.
							O.H. : 830, T. : 650	285	10	450	100	38, 45	46, 48	,,
9	0·25	0·48	3·05	0·03	nil.	—	Normalised 800-850	203	5	450	100	25, 27	16, 17	37
10		3 per cent. nickel steel.					Unknown.	241	8	400	200	48, 52	6, 6	88
11		,,					,,	237	8	400	200	51, 52	11	80
12	0·25	0·55	4·9	0·08	trace.	—	Normalised 800-850	181	5	450	100	41, 42	48, 50	nil.
13	0·125	0·53	0·05	trace.	0·4	0·47	Normalised 900	132	5	450	200	49, 55	16, 17	68
14	0·34	1·51	0·09	0·03	nil.	—	O.H. : 850, T. : 650	—	10	450	125	27, 31	15, 18	43
15	0·50	0·57	nil.	1·04	,,	—	O.H. : 850, T. : 700	223	5	450	200	42, 44	44, 45	nil.
16	0·46	0·59	,,	1·05	0·8	—	O.H. : 850, T. : 700	248	5	450	200	39, 40	39, 40	,,
17	0·48	0·63	,,	2·05	0·24	—	O.H. : 850, T. : 700	262	5	450	200	43, 44	40, 42	5
18	0·50	0·64	,,	1·04	nil.	Va 0·22	O.H. : 850, T. : 700	241	5	450	200	40, 41,	43, 41	nil.

TABLE 5.

Results Obtained in the Imperial Chemical Industries Research Department, Billingham.

No.	Composition of Steel. Per Cent.					Heat Treatment °C. O.Q. = Oil Quenched. A.C. = Air Cooled. W.Q. = Water Quenched.	Embrittling Treatment.			Impact. Ft.-lb.		Reduction Impact Value. Per Cent.
	C.	Cr.	Ni.	Mo.	Other Alloying Elements.		Stress. Tons/sq. in.	Temp. °C.	Time Cycles.	Initial Condition.	After Treatment.	
1	0·25	12–14	—	—	—	O.Q. : 950	10	390	50	11·5, 12, 11, 12	12·5, 12·5, 12·5	nil.
						A.C. : 700	10	450	50	—	11·5	
2	0·20–	1·25	3·76	—	—	O.Q. : 830	10	390	50	39·5, 41, 37·5	10·5, 21	50–75
	0·30					O.Q. : 600–650	10	450	50	38·5	5·5	87
3	0·35	1·13	0·45	—	0·15 V	O.Q. : 850	10	390	50	18, 25·5, 17·5	16, 25·5, 11·5	8–37
						W.Q. : 560	10	450	50	23	10·5	40–60
4	0·28	0·87	3·60	0·24	—	O.Q. : 820	10	390	50	55, 54·5, 56	31, 30·5, 8	43–48
						A.C. : 640	10	450	50	58·5	14·5	73–76
5	0·30	0·60	2·5	0·60	—	As received from	10	390	50	31·5, 34, 31·5	31, 31·5, 29, 27	nil.
						makers.	10	450	50	33	—	,,
6	0·20	—	—	—	—	Normalised.	10	390	50	37, 32·5, 36·5	19, 21·5	33–48
							10	450	50	32	21·5, 20·5	33–45
7	0·20	—	—	—	—	,,	10	250	50	37, 32·5, 36·5	16, 13, 17, 12·5	47–66
8	0·61	8·32	—	—	2·62 Si	O.Q. : 1000	10	390	50	8·5, 9·5, 10·5	8·5, 9·5	nil.
						W.Q. : 825	10	450	50	10	7·5, 8·5	,,
9	0·30	1·12	—	0·28	—	O.Q. : 850	10	390	50	33, 31·5, 31·5	30·5	,,
						O.Q. : 600	10	450	50	—	33, 35	,,
10	0·20–	0·97	3·66	—	—	O.Q. : 830	10	390	50	28, 29	25, 27·5	0–13
	0·30					O.Q. : 600–650	10	450	50	—	7, 8	72–76
11	0·12	18	8	—	0·6 W	W.Q. : 1150	10	390	50	—	90·5, 79	nil.
							10	450	50	87	88, 80	,,
12	0·25	0·57	—	0·51	—	O.Q. : 900	10	400	50	29, 27·5, 28	19, 20	27–35
						A.C. : 650	10	450	50	29	16, 33	42–45
13	0·25	0·57	—	0·51	—	A.C. : 900	10	450	50	21, 17·5, 23·5	12, 17	3–49
						A.C. : 650	10	450	50	19	10·5, 19·5	40–55
14	—	—	3·1	—	—	—	10	400	50	28, 29	11, 25	10–62
							10	450	50	—	22·5, 13	22–55
15	0·12	—	—	0·35	—	Normalised.	10	400	50	27·5, 21	15·5, 16	24–44
							10	450	50	—	20·5, 16·5	0–40
16	0·34	0·82	0·65	1·10	—	O.Q. : 830	10	370	50	26, 28	29, 32	nil.
						O.Q. : 650	10	450	50	—	29, 29·5	,,
17	0·28	0·87	3·60	0·24	—	O.Q. : 820	0	400	50	55, 54·5, 56	35, 34·5	35–41
						A.C. : 640	0	450	50	58·5	32·5, 31	40–47
18	0·32	0·95	3·80	—	—	O.Q. : 830	10	—	—	—	—	—
						O.Q. : 620	10	370	50	40	26·5	34
19	0·30	0·60	2·5	0·60	—	As received from	10	390	150	31·5, 34, 31·5	33·5, 31·5	nil.
						makers.	10	450	150	33	28·5, 27·5	10–20

The following experiment, carried out by Bailey and Roberts (*Proc. Inst. Mech. Eng.*, 1932, **122**, 209), clearly demonstrates this point :—

Embrittlement Treatment.	Yield Point. Tons/sq. in.	Ult. Tensile Stress. Tons/sq. in.	Elongation. Per Cent.	Red. of Area. Per Cent.	Izod Test. Ft.-lbs.
Nil . . .	56	62·9	24	64	59
450° C. and stress of 5 tons per sq. in. for 250 hours .	55·4	63	22·8	59	13

The steel used was of the following composition :—

C	Si	Mn	P	S	Ni	Cr	Mo
0·34	0·20	0·64	0·029	0·025	3·34	0·22	0·21

A careful survey of the tables will show that molybdenum, if present in appropriate amounts, i.e. not less than 0·6 per cent., is very effective in preventing this " temper brittleness " form of embrittlement.

Quite apart from the " temper brittleness " type of embrittlement, there is another kind associated with steels of the stainless austenitic high chromium-nickel type when these are subjected to tensile stresses within the region 500-850° C. There appears to be some connection between this embrittlement and the precipitation of carbide in the form of a membrane surrounding the austenitic grains, thereby producing intergranular weakness. Another point is that many of these austenitic corrosion resisting steels lose their corrosion resisting properties when held at temperatures of 400-900° C. for a little time, and this is particularly the case with the 18 : 8 type. This point is discussed at length by Elliot, Sarjant and Cullen (*J.S.C.I.*, 1932, **51**, 502). Apparently the only element which serves any useful purpose in this connection when added to the 18 : 8 alloys is titanium, and when present in amounts of the order of 1 per cent. seems to have quite a beneficial effect in preventing excessive embrittlement in service.

Use of Published Creep Data in Fixing Working Stresses.

With regard to the use of creep data for fixing permissible working stresses, to avoid the long time tests necessary for the estimation of the true limiting creep stress, which involves test periods of many months, Dr. W. H. Hatfield of the Brown Firth Research Laboratories, has introduced a test involving short-time creep tests over a period of four to five days to find what he describes as the " time yield " of the material in question. He defines this time yield as " the stress within which, at the temperature desired, stability of dimensions is reached within a period of twenty-four hours, for a further period of forty-eight hours, with an extension not exceeding the elastic deformation of 0·5 per cent. on the gauge length, with limitations as regards measurement for permanence of dimensions of one-millionth of an inch per inch per hour." The table gives particulars of four structural steels, and their " time-yield " curves are shown in Fig. 161.

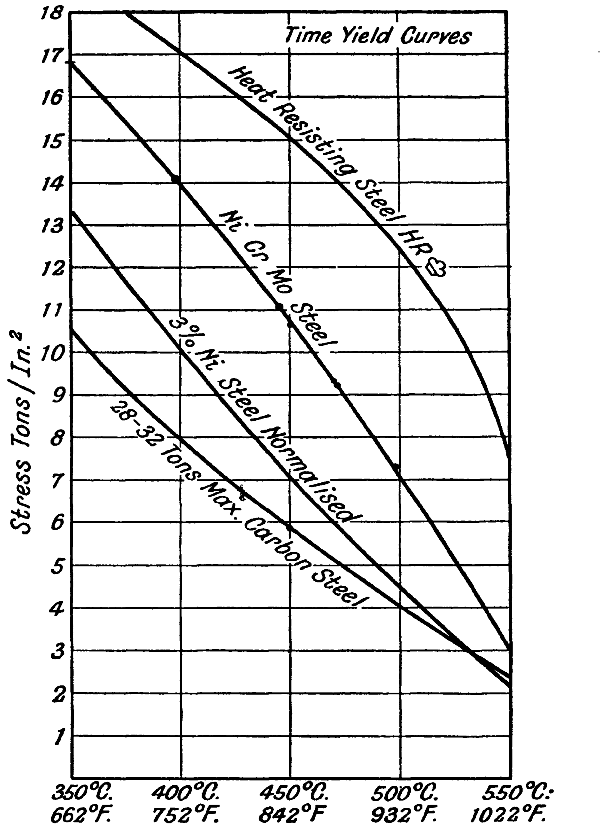


FIG. 161.—Hatfield's " time-yield " curves.

	C.	Mn.	Si.	Ni.	Cr.	Mo.	W.	Condition.
Mild steel .	·25	·58	·11	·13	—	—	—	Normalised 900° C.
Nickel steel .	·24	·55	·20	3·3	—	—	—	Normalised 850° C.
Ni-Cr-Mo steel .	·30	·57	·24	2·38	·61	·59	—	O.H. 850 T. 620/30° C.
Heat resisting steel . .	·50	·60	·50	9·4	12·68	—	3·75	Air cooled 1000° C.

Tables 6 and 7 show the ordinary tensile test figures and the " time yield " for a number of other representative alloy and carbon steels (W. H. Hatfield, *J. Iron and Steel Inst.*, 1930, **122**, 215).

TABLE 6.

RUST, ACID, AND HEAT RESISTING STEELS.

Steel.	Condition.	Analysis.						Tensile Tests at 15° C.				Time Yield. Tons/sq. in.						
		C.	Mn.	Si.	Cr.	Ni.	W.	Yield Point. Tons/sq. in.	Max. Stress. Tons/sq. in.	Elong. Per Cent.	Reduction of Area. Per Cent.	200° C.	300° C.	400° C.	500° C.	550° C.	600° C.	700° C.
Silicon-chromium . .	O.H. 950° C., T. 750° C. . .	0·51	0·38	3·16	8·26	0·16	—	46·9	60·2	26·7	54·9	—	—	19·00	2·5	—	—	—
Stainless	A.C. 1000° C., T. 700° C. . .	0·15	0·36	0·81	14·66	0·19	—	33·4	45·1	32·0	54·0	—	—	14·75	6·0	—	—	—
Stainless	O.Q. 975° C., T. 750° C. . .	0·29	0·28	0·30	13·04	0·35	—	36·0	48·0	29·0	59·0	—	25·0	14·5	5·75	—	—	—
18 per cent. chromium-nickel	Softened 1150° C.	0·16	0·30	0·29	17·82	8·04	—	15·7	44·1	57·0	59·2	10·0	7·75	6·75	6·2	3·0	—	—
Nickel-chromium-tungsten	Softened 1050° C.	0·51	0·63	0·40	12·64	9·81	3·75	26·0	56·2	32·0	40·5	—	—	19·5	12·6	7·5	4·2	2·0
High-speed tool steel .	Annealed 900° C.	—	—	—	—	—	—	45·5	57·7	9·3	14·0	—	—	—	6·25	4·0	2·3	—
	Hardened 1320° C. T. 600° C. for 3 hours . .	0·74	0·23	0·42	3·82 Co 4·15	—	18·06 V 1·18	—	—	—	—	—	—	—	22·0	—	3·0	—

TABLE 7.

Carbon and Ordinary Alloy Steels.

Steel.	Condition.	Analysis.								Tensile Test at 15° C.				Time Yield. Tons/sq. in.			
		C.	Mn.	Si.	Ni.	Cr.	Mo.	V.	Al.	Yield Point. Tons/sq. in.	Max. Stress. Tons/sq. in.	Elong. Per Cent.	Reduction of Area.	300° C.	400° C.	500° C.	550° C.
Mild carbon . . .	Normalised 890-900° C. . .	0·25	0·58	0·11	0·13	—	—	—	—	20·6	33·9	30	63·0	13·5	8·1	4·2	2·3
	Annealed 660° for 48 hours .									16·5	29·8	32·0	60·0	—	6·3	3·5	1·68
Higher carbon . . .	Normalised 850° C.	0·33	0·58	0·21	0·20	—	—	—	—	23·5	38·2	28·0	60·7	—	8·1	4·5	2·5
3 per cent. nickel low carbon	Normalised 850° C.	0·24	0·55	0·20	3·3	nil.	—	—	—	26·2	40·85	26·4	62·6	—	10·2	4·7	2·1
Nickel-chromium-molybdenum-vanadium . .	O.H. 850° C., T. 650° C. for 3 hours . .	0·25	0·63	0·23	3·10	1·35	0·55	0·22	—	54·4	60·0	22·5	70·4	—	18·0	7·5	2·9
Chromium-aluminium .	O.H. 850° C., T. 650° C. for 3 hours . .	0·46	0·59	0·27	0·07	1·72	0·33	—	1·01	58·4	67·6	16·5	53·0	—	16·5	5·5	2·2

TABLE 8.

LIMITING CREEP STRESS AND SHORT-TIME TENSILE PROPERTIES.

Material.	Temperature °C.	Limiting Creep Stress based on Creep Rate of 10^{-5} in./in./day. Tons/sq. in.	Primitive Limit of Proportionality. Tons/sq. in.	Proof Stress based on 0·05 per cent. Permanent Set. Tons/sq. in.		Short-time Ultimate Stress. Tons/sq. in.
0·3 per cent. carbon cast steel, annealed	Air	—	8·0	—	0·1 per cent. permanent set.	31·0
	400	10·0	4·4	10·4		28·5
	500	4·0	—	9·7		20·0
0·39 per cent. carbon forged steel, annealed.	Air	—	14·5	—	0·1 per cent. permanent set.	40·5
	400	13·0	4·4	14·0		36·5
	500	5·0	2·6	12·2		26·5
0·51 per cent. carbon steel, hardened and tempered (600° C.).	Air	—	27·4	—		44·1
	300	29·6	11·6	23·0		48·0
	400	15·4	10·3	20·0		34·5
	500	2·7	4·0	15·0		23·0
1·7 per cent. manganese steel, normalised.	Air	—	16·8	—	0·1 per cent. permanent set.	39·5
	300	28·0	9·2	11·5		43·5
	400	15·9	5·8	10·0		35·9
	500	5·0	2·1	7·0		27·5
	600	0·7	1·1	4·5		16·0
3·4 per cent. nickel steel hardened and tempered (600° C.).	Air	—	22·8	—		47·8
	300	32·0	14·0	—		48·7
	400	13·0	10·0	—		37·6
	500	2·7	4·6	—		25·4
Nickel-chromium steel, 3·5 per cent. Ni, 0·24 per cent. Cr, heat-treated.	Air	—	18·0	—		48·0
	300	30·3	14·0	27·3		49·0
	400	7·6	9·0	22·8		38·0
	500	1·5	4·4	16·8		27·3
	600	0·4	—	7·6		16·6

Chrome-vanadium steel, 1·18 per cent. Cr, 0·25 per cent. V, heat-treated.	Air	—	33·0	—		65·0
	300	47·0	30·3	42·6		60·7
	400	18·2	15·8	37·4		52·3
	500	1·9	5·0	28·2		41·5
NiCrMo steel, 2·96 per cent. Ni, 1·11 per cent. Cr, 0·49 per cent. Mo.	Air	—	26·0	—	0·01 per cent. permanent set.	64·6
	450	15·5	11·7	22·9		49·6
	500	6·6	—	—		—
	550	1·0	5·5	10·8		36·2
MoCrCu steel, 0·94 per cent. Mo, 0·43 per cent. Cr, 0·37 per cent. Cu.	450	23·8	about 3·6	10·4	0·1 per cent. permanent set.	30·8
	500	14·3	,, 3·6	10·1		29·1
	550*	6·5	,, 3·2	10·0		27·3
Stainless steel, 13 per cent. Cr, heat-treated.	Air	—	24·0	—		48·0
	300	31·5	22·0	27·2		42·0
	400	19·5	14·0	25·0		38·0
	500	4·5	5·0	20·5		30·6
	600	0·8	—	11·2		20·5
18 : 8 chrome-nickel steel, softened.	Air	—	8·0	—		51·6
	400	30·2	2·8	6·6		32·2
	500	8·0	—	6·2		29·8
	600	5·5	—	6·0		26·0
High-speed steel, 16·8 per cent. W, 3·7 per cent. Cr, 1 per cent. V, as rolled.	Air	—	—	—		51·7
	600	4·3	4·0	—		24·9
	700	1·6	—	—		15·8
	800*	about 0·6	—	—		8·4
26 : 16 NiCr steel, as rolled.	Air	—	—	—		47·3
	600	4·9	4·0	—		32·9
	700	2·1	3·2	—		25·0
	800*	0·6	—	—		14·5
14 : 14 : 2 NiCrW steel, as rolled.	Air	—	—	—		56·7
	600	6·3	—	—		35·5
	700	2·6	—	—		26·1
	800*	1·0	—	—		17·0

* Intercrystalline cracking observed at these temperatures.

Barr and Bardgett (*Proc. Inst. Mech. Eng.*, 1932, **122**, 285) also suggest an accelerated test for determining the permissible working stress of materials for high temperature service. They carried out many creep tests, depending on the measurement of the diminishing rate of creep in a strained test piece by means of a steel weigh bar so that the creep of the test piece is accompanied by a proportional decrease in the applied stress. The period of test was forty-eight hours.

Other workers in this field (e.g. Tapsell, Bailey and Roberts, and Lea) do not regard these short-time tests as quite representative of what may happen if the tests are prolonged because slow structural change in the steel may cause different creep rates with lapse of time. Tapsell, for example, suggests long-time creep tests in which the creep limit is based on a rate of creep of 10^{-5} in. per in. per day at 40 days, and Table 8 shows creep data on this basis for many steels used in high-temperature service.

Tables 9 and 10 (pp. 237 and 238) give particulars of the creep of carbon and alloy steels also found from long-time creep tests.

Non-ferrous Metals at High Temperature.

Tapsell and Bradley (*J. Inst. Metals*, 1926, **35**, 75) found that the limiting creep stress of Ni 68·7, Cu 28·2, Fe 0·56, Mn 2·35, a nickel-copper alloy rolled bar, was 24·0 tons/sq. in. at 400° C., and that at higher temperatures, 500° C., failure occurred not on account of creep, but primarily because of severe intercrystalline cracking. A nickel-chrome alloy (Ni 79·7, Cr 19·0, Fe 0·88), again in rolled bar form, has a limiting creep stress of 24·0 tons/sq. in. at 500° C., but at higher temperatures failure under stress is due to intercrystalline cracking.

Cournot and Pagès (*Rev. de Mét.*, 1926, **23**, 701) found that annealed copper begins to lose strength at 100° C., and that the strength at 250° C. is half that at ordinary temperature. At 400° C. this material is entirely plastic under very low stress. National Physical Laboratory tests on rolled brass bar (Cu 59·8, Zn 38·6, Pb 0·99, Sn 0·34) show that this material has a limiting creep stress of 0·4 tons/sq. in. at 250° C., and that a rolled phosphor bronze bar (Cu 94·26, Sn 5·49, P 0·24) has a limiting creep stress of 4·4 tons/sq. in. at 250° C., and 1·0 tons/sq. in. at 350° C.

TABLE 9.

STRESSES PRODUCING 0·1 PER CENT. DEFORMATION IN 1000 HOURS. (FRENCH, KAHLBAUM AND PETERSEN.)

Material.	Analysis.						Condition.	Stresses. Tons/sq. in.			
	C.	Mn.	Si.	Ni.	Cr.	W.		700° F.	1000° F.	1200° F.	1360° F.
Ni-Cr Alloy	0·31	2·79	0·27	76·0	18·8	—	A.C. 1900° F.	—	2·23	0·63	
Ni-Cr-Fe Alloy	0·25	1·4	0·06	60·8	10·75	2·8	Ann. 1470° F.	—	5·35 (985° F.)	3·9 (1215° F.)	2·6 (1370° F.)
,, ,,	0·19	1·62	0·10	57·6	10·28	3·19	As rolled	—	14·7 (990° F.)	2·8	0·22
,, ,,	0·32	1·52	0·03	34·9	12·93	—	,,	—	10·3 (990° F.)	4·0	0·22
,, ,,	0·28	1·5	0·07	38·6	10·64	1·77	,,	—	11·6 (990° F.)	2·23 (1185° F.)	—
Ni-Cr-W Steel	0·29	0·50	1·18	8·0	19·86	4·5	Forged	—	10·3 (995° F.)	5·35 (1160° F.)	1·9 (1390° F.)
18 : 8 Steel	0·15	0·35	0·22	8·46	17·32	—	Rolled	—	4·9 (990° F).	4·45 (1165° F.)	2·23 (1380° F.)
Cr-V ,,	0·40	0·57	0·25	—	2·26	0·20 (V)	A.C. 1375° F.	—	1·34	0·13	
Carbon Steel	0·23	0·48	0·18	0·05	—	—	F.C. 1330° F.	4·24			
,, ,,	0·45	0·55	0·15	0·24	—	—	F.C. 1330° F.	8·47			
Ni Steel	0·37	0·68	0·21	3·46	—	—	F.C. 1330° F.	7·7			
Ni-Cr Steel	0·36	0·63	0·19	1·25	0·62	—	F.C. 1280° F.	11·6			
,, ,,	0·35	0·49	0·19	1·66	0·99	—	F.C. 1320° F.	9·15			

A.C. = Air cooled. Ann. = Annealed. F.C. = Furnace cooled.

TABLE 10.

STRESSES CORRESPONDING TO 0·1 PER CENT. DEFORMATION IN 10,000 HOURS. (KANTER AND SPRING.)

Tons per square inch.

Composition.						Condition.	Temperature °F.					
C.	Si.	Mn.	Ni.	Cr.	Mo.		550.	750.	800.	900.	1000.	1200.
0·33	0·34	0·77	—	—	—	Cast—Annealed	—	6·5	—	1·3	0·8	0·45
0·40	0·32	0·70	—	—	—	,, ,,	6·3	4·8	—	2·0	0·9	—
0·20	0·24	0·60	—	—	—	,, ,,	12·5	—	3·3	—	—	—
0·20	0·24	0·60	—	—	—	Forged—Annealed	13·4	3·7 (760° F.)	—	—	—	—
0·35	0·06	0·64	—	—	—	Rolled—Normalised	9·8	—	3·3	—	0·6	—
0·17.	0·02	0·47	—	—	—	Rolled—Normalised	5·8	—	3·2	—	0·9	—
0·41	0·06	0·53	—	—	—	Forged—Normalised	—	—	3·1	—	—	—
0·40	0·28	0·57	2·03	0·82	—	Cast—Heat-treated	23·8	—	6·3	1·7	0·7	—
0·46	0·25	0·56	1·34	0·50	—	Quenched—Tempered	11·9	—	1·4	—	—	—
0·41	0·29	0·58	2·00	0·87	—	Cast—Heat-treated	25·4	—	8·9	—	1·8	—
0·41	0·29	0·58	2·00	0·87	—	Forged	—	—	3·1	—	0·8	—
0·37	0·24	0·48	—	0·91	0·24	Quenched—Tempered	24·6	—	4·0	—	1·2	—
0·12	0·32	0·56	—	12·23	—	—	—	—	5·2	—	1·2	—
0·10	0·43	0·51	9·35	19·82	—	Forged	—	—	—	—	7·0	2·4
0·57	0·97	0·33	—	6·44	W 6·63	Quenched—Tempered	—	—	7·7	—	2·4	—

The following tables which give particulars of long-time creep tests on a 6 per cent. Cr, 0·5 Mo or W steel have been very kindly supplied by the Engineering Division of the University of Michigan. As will be seen later, this steel is one of the best types to use for high-temperature service when handling hydrogen under high pressure, and hence these authoritative creep data are of considerable value.

TABLE 11.

SHORT-TIME TENSILE PROPERTIES AT ELEVATED TEMPERATURES OF A 0·10 C, 0·18 Si, 0·45 Mn, 5·09 Cr, 0·55 Mo STEEL.

Temperature.	Tensile Strength. Lb./sq. in.	Yield Stress. Lb./sq. in.	Proportional Limit. Lb./sq. in.	Elongation. Per Cent. in 2 ins.	Reduction of Area. Per Cent.
85° F.	66,575	25,400	19,000	39·0	80·5
750° F.	51,775	20,150	14,000	30·25	76·7
900° F.	48,350	18,200	11,500	28·5	76·85
1000° F.	44,465	16,750	7,500	28·5	73·5
1100° F.	34,375	14,900	6,000	38·75	87·3
1200° F.	25,800	11,000	1,500	46·0	91·0
1300° F.	19,075	8,650	1,750	65·0	94·55
1400° F.	13,275	6,500	1,500	65·0	95·9

Investigations sponsored at the University of Michigan by The Timken Steel and Tube Company.

(*Author's Note.*—Heat treatment of above not given, but presumably it has been annealed from 1500-1600° F. to give the mechanical properties stated. This applies to all tables supplied by the University of Michigan on these Cr-Mo and Cr-W steels.)

TABLE 12.

CREEP CHARACTERISTICS AT 800, 1000 AND 1200° F. OF A 0·10 C, 0·18 Si, 0·45 Mn, 5·09 Cr, 0·55 Mo STEEL.

Temperature.	Stress for Designated Rate of Creep Rate = Per Cent. per 100,000 Hrs. Lb./sq. in.	
	1·0	10·0
800° F.	14,250	22,000
1000° F.	7,000	10,250
1200° F.	900	2,500

Investigations sponsored at the University of Michigan by The Timken Steel and Tube Company.

TABLE 13.

CHARPY IMPACT RESISTANCE AT ELEVATED TEMPERATURES OF A 0·10 C, 0·18 Si, 0·45 Mn, 5·09 Cr, 0·55 Mo STEEL.

Temperature.	Charpy Impact Resistance. Foot-Pounds.
85° F.	81·0
500° F.	68·5
600° F.	72·5
750° F.	75·0
900° F.	64·5
1000° F.	58·5
1100° F.	54·5
1200° F.	53·5

Investigations sponsored at the University of Michigan by The Timken Steel and Tube Company.

TABLE 14.

SHORT-TIME TENSILE PROPERTIES AT ELEVATED TEMPERATURES OF A ·08 C, ·20 Si, ·42 Mn, 4·88 Cr and 1·10 W STEEL.

Temperature.	Tensile Strength. Lb./sq. in.	Yield Stress. Lb./sq. in.	Proportional Limit. Lb./sq. in.	Elongation. Per Cent. in 2 ins.	Reduction of Area. Per Cent.
75° F.	66,500	25,000	15,000	36·0	71·4
800° F.	50,400	—	11,250	26·0	63·5
900° F.	46,950	—	10,000	26·0	73·5
1000° F.	41,250	—	8,750	32·0	78·3
1100° F.	34,500	—	7,500	38·0	85·8
1200° F.	21,875	—	6,250	37·0	91·7

Investigations sponsored at the University of Michigan by The Timken Steel and Tube Company.

TABLE 15.

CREEP CHARACTERISTICS AT 1000° F. OF A ·08 C, ·20 Si, ·42 Mn, 4·88 Cr and 1·10 W STEEL.

	Stress for Designated Rate of Creep Rate = Per Cent. per 100,000 Hrs. Lb./sq. in.	
Temperature.	1·0	10·0
1000° F.	5,650	8,400

Investigations sponsored at the University of Michigan by The Timken Steel and Tube Company.

From these tables it will be apparent that there are considerable differences in the methods of obtaining creep data, and also in the evaluation of such data in fixing permissible working stresses.

In this connection it is to be noted that most of the data available on creep are based upon simple tensile tests, and such ideally simple stress conditions rarely, if ever, obtain in practice. Hence, whatever basis is used, a reasonably generous interpretation of creep results is desirable, and due allowance made for the complexity of stress distribution under operating conditions.

Insofar as carbon steels are concerned, accumulated experience has shown that medium carbon steel (0·25 per cent. C) of good quality may be safely stressed in accordance with the following table :—

Tons/sq. in.

350° C.	400° C.	425° C.	450° C.	475° C.
5·0	4·0	3·25	2·5	2·0

For high-pressure vessel work, carbon steel should not be used at temperatures much higher than 440° C. For low carbon steels (0·15 per cent. C), a figure 20 per cent. less than those given in the table may be safely employed, and for 0·45 carbon steels a stress 20 per cent. greater than the above, provided, of course, that in all cases the calculated stress is a true representation of actual working conditions, and that the designed working temperature is not likely to be exceeded in practice. If wide fluctuations in temperatures are at all likely (e.g. super-heater tubes of large water tube boilers), due allowance must, of course, be made in this respect.

In the case of alloy steels, the position is not quite so well defined. Experience with vessels of alloy steels is confined to the past dozen years or so, and not much comparative data have been published. Insofar as experimental plant is concerned, I have used Dr. Hatfield's "time-yield" figures as the basis of design in all plant built at the Chemical Research Laboratory from new alloy steels, with quite satisfactory results. There is no doubt that for experimental work when new steels are being tried out under actual working conditions such a basis is most useful, since time-yield figures can be obtained in a few days. If experimental results warrant the use of the steel on commercial scale, long-time tests for creep and stability can then be put in hand before finally committing oneself to the considerable expenditure involved.

As an example of the stresses suggested for alloy steel, based on long-time creep tests, Tapsell recommends that a factor of safety of at least two but more generally three on the limiting creep stress (10^{-5} in. per in. per day), as given in Tables 8 and 2, be used in actual practice, whereas Hatfield suggests two-thirds of his "time-yield" figures.

Corrosion and Hydrogen Penetration of Steels at High Temperatures.

We have so far discussed the suitability of various steels and alloys for high-temperature service from the mechanical standpoint, i.e. resistance to plastic deformation and embrittlement when under working conditions. There remains the corrosion resisting properties of otherwise satisfactory materials.

Corrosion may affect the problem in one or more different ways. Firstly there is external corrosion of vessels or components, when exposed to the corrosive influence of furnace gases, i.e. where the agent is oxygen either as atmospheric oxygen or as a constituent of the products of combustion of fuel. Hence the oxidising agents are mainly steam and the oxides of sulphur and carbon.

The second aspect of corrosion is that of resistance to the chemical attack of the reagents within the pressure vessel under the desired working conditions. Obviously, no general recommendations can be made, as each problem will have its own peculiar characteristics, but a great deal of useful data in this respect will be found in the paper by Elliot, Sarjant and Cullen to which reference has just been made, and in Monypenny's book, " Stainless Iron and Steel " (Chapman & Hall, 1932).

The final, and perhaps from a chemical engineering point of view, the most important aspect of corrosion in many high-pressure processes is the effect of hydrogen and other gases upon the stressed walls of high-temperature vessels.

That the severe working conditions of the ammonia synthesis affect the structural parts of the pressure plant exposed to high temperatures was soon recognised by the Badische Anilin in the early stages of the commercial development of the Haber-Bosch process.

The following English patents are of interest in this connection :—

20,127. *Catalyst chambers for ammonia synthesis.*

Badische Anilin und Soda Fabrik. August, 1910.

Loss of strength of the walls of the vessel, which withstand the pressure and are heated to a temperature approaching that at which the catalyst union of nitrogen and hydrogen takes place, is avoided if the walls do not come into contact with gases which contain more ammonia than the quantity that corresponds to the state of equilibrium which exists at the wall. This can be effected by enclosing the catalytic materials in an inner tube and passing the gases through the space between the vessel and the inner tube and then through the catalytic material.

1490. *Catalyst chamber for high-pressure synthesis of ammonia.*

Badische Anilin und Soda Fabrik. January, 1912.

To enable apparatus employed in operations using hydrogen at high pressure and temperature to withstand the pressure, the inner tube or vessel is supported at all parts at which it is subjected to the hot hydrogen, and these means are arranged to allow any diffusion gas to escape, without acting under pressure thereon.

29,260. *Catalyst tubes for ammonia synthesis.*

Badische Anilin und Soda Fabrik. December, 1912.

Tubes or vessels employed at high temperatures in ammonia synthesis are constructed of iron, with which is alloyed a metallic solidity-giving element such as chromium, vanadium, tungsten or molybdenum. It is immaterial whether the alloy contains carbon or not, provided that the remaining alloy after the removal of carbon possesses sufficient mechanical solidity. The use of high nickel alloys should be avoided.

28,200. *Catalyst tubes for ammonia synthesis.*

Badische Anilin und Soda Fabrik. December, 1912.

Iron vessels used for carrying out operations, in which hydrogen under pressure and high temperature is employed, are arranged so that an atmosphere of nitrogen gas is interposed between the hydrogen or mixture containing hydrogen and the hot pressure sustaining wall of the vessel. This can be effected by providing a pervious lining, which may be made of iron, and passing nitrogen into the space between the lining and the vessel.

Quite apart from experience gained from the ammonia synthesis, it has long been known that when ordinary carbon steel is subjected to the influence of hydrogen when at a red heat, the carbon in the steel is gradually removed by the hydrogen, with the probable formation of methane, and this effect has recently been shown to increase very rapidly with increase of pressure and temperature. (For example, even at ordinary temperature Bridgman found that small steel pressure vessels with substantial walls were quite pervious to hydrogen at pressures of several thousand atmospheres.) The decarbonisation of the steel is also accompanied by cracking and fissuring of the steel, and general weakness and embrittlement results. This problem has been quite formidable, and in view of the importance of hydrogenation work, a great deal of research has been carried out, as will be seen from the patent abstracts at the end of this chapter.

An interesting report in this connection is that of the examination of a reaction vessel used at the Fuel Research Station at Greenwich for the hydrogenation of coal by the Bergius process. The reaction vessel was made from mild steel, 8-in. internal diameter, with walls $2\frac{5}{8}$-in. thick, and after about 700 working hours the vessel failed by a longitudinal crack right through the metal, and the contents were ejected with considerable force. The working conditions were 200 atms. at temperatures of 475° C., or so, and upon examination of the steel it was found that it was practically denuded of carbon, while hydrogen had been absorbed by the steel to the extent of 1·8 c.c. of hydrogen per gram of steel. This remarkable result will show the difficulties which have been encountered in the development of the Bergius process.

A series of experiments of great interest in connection with the synthetic ammonia process has been carried out by Vanick (*Chem. Met. Eng.*, 1927, **34**, 489) in which he subjected different steels to the action of a mixture of hydrogen, nitrogen and ammonia under high-pressure and high-temperature conditions. The conclusions he reached from early experiments were as follows :—

(1) The removal of elements such as carbon or oxygen or their compounds through reaction with hydrogen encourages voiding and fissuring, while the presence of chromium in forming more stable nitrides, and retarding the diffusion and penetration of the gas, assists in retarding deterioration.

(2) Fissuring is induced by dissolved hydrogen made soluble by activation from infiltration through the metal or by release from the ammonia which is rendered unstable in contact with the catalytic metal surfaces.

(3) The more rapid diffusion and effusion of hydrogen in contrast to the other gases of the mixture permits an ammonia enrichment to the extent of developing a localised super-equilibrium, with alternate formation and decomposition of nitrides as a result.

Resistance to corrosion by an alloy of chromium-nickel-silicon and iron suggested further tests of a number of chromium steels and alloys. Test conditions were chosen to simulate operating conditions in the synthesis of ammonia, i.e. 100 atms. 500° C. and an ammonia concentration of 8·3 per cent. in a gas containing hydrogen and nitrogen in the proportion of $N_2 : 3H_2$. The test specimens were in the form of cylinders, one for each steel or alloy, and each had an internal volume sufficiently large to accommodate two tensile, two Charpy impact and two corrosion specimens of the usual shape and having the same composition and preliminary treatment as the cylinder. These specimens were, therefore, exposed on all sides to attack, but were not stressed as were the cylinders by the internal pressure of the gas mixture. Each material was to be exposed until failure of the cylinder occurred or deterioration had reached such a point that further exposure would lead to but little additional information (see Table 16).

Very little change occurred in the various steels during the first two weeks or so. With longer exposure fissures and decarbonisation occurred. Two types of penetration were observed, the uniform concentric inward migration and the selective or tendril type of advance, the latter being harder to detect or evaluate and consequently more dangerous.

Preliminary conclusions were as follows :—

(1) Low carbon steels appear to suffer less deterioration than high carbon steels.
(2) Nickel steels show a distinctive type of selective fissuring, reaching to the core of the specimen in some of the four months' exposures.
(3) Chromium steels within the low range of chromium studied in the series also suffer from the treacherous tendril form of penetration. It appears that high chromium contents offer greater resistance to penetration, while higher carbon contents permit greater fissuring and voiding in the penetrated zone.
(4) Nickel chromium steels reflect the influence of both elements.
(5) A tungsten chromium steel is apparently the least affected in any of the groups chosen ; except for the intergranular fissures close to the surface of this specimen, very little evidence of attack was available. This composition is undoubtedly superior to its companions, notwithstanding an initially high carbon content.

The improvement shown by an ordinary chrome-vanadium steel over steels previously tested suggested even better results by varying the three alloying elements in it, namely, carbon, chromium and vanadium ; because of the commercial availability of the chrome-vanadium steel it was decided to follow this lead. The composition chosen therefore represented three series, in each of which one of the elements is varied and the other two are constant. Two steels of the stainless type were added, and samples of the commercial 0·3 per cent. carbon-chrome-vanadium steel used in the first series were included for comparison.

Results of Final Tests.

The conditions were ten months' exposure to hydrogen-nitrogen ammonia mixture as before at 500° C. and 100 atms. A group of fourteen steels was chosen to cover variation of the carbon, chromium and vanadium contents of an ordinary chrome-vanadium steel within the limits of 0-1·2 per cent. C., 0-14·0 per cent. Cr and 0-0·65 per cent. V, and the results showed that :—

(1) The carbon content must be low.
(2) Two or more per cent. of chromium is necessary to confine the fissuring and decarbonisation to a smooth and uniform penetration.
(3) A suitable steel would contain at least 2·25 per cent. Cr, and not more than 0·3 per cent. C.
(4) Larger quantities of chromium improve the resistances further, but not in proportion to the increase in chromium.
(5) High chromium and chrome-nickel steels of the stainless type are most resistant.
(6) Heat treatment is useful to dissolve the alloys in steel inherently resistant, but adds little or no improvement to partly successful steels.
(7) Vanadium adds no appreciable improvement.
(8) The chief features of the attack of the gases upon the steels were represented by (*a*) decarbonisation, (*b*) sharp increase in combined nitrogen, chiefly in the chromium steels, (*c*) fissuring and porosity in the affected zones, (*d*) lowered strength and ductability.

TABLE 16.

Per Cent. Composition of Steels used in First Series of Tests.

C.	Mn.	P.	S.	Si.	Cr.	Ni.	V.	W.
·19	·43	·008	·033	·17	—	—	—	—
1·01	·40	·007	·036	·16	—	—	—	—
·24	·52	·008	·032	·03	—	3·43	—	—
·30	·68	·012	·024	·26	·93	—	0·18	—
·39	·70	·011	·044	·29	·84	3·56	—	—
·27	·59	·014	·022	·13	1·00	1·60	—	—
·93	·30	·010	·014	·21	1·47	—	—	—
·48	·79	·030	·029	·23	·60	—	—	—
·58	·36	·004	·017	—	·55	·21	—	1·62
·10	·31	·008	·023	·31	—	4·87	—	—

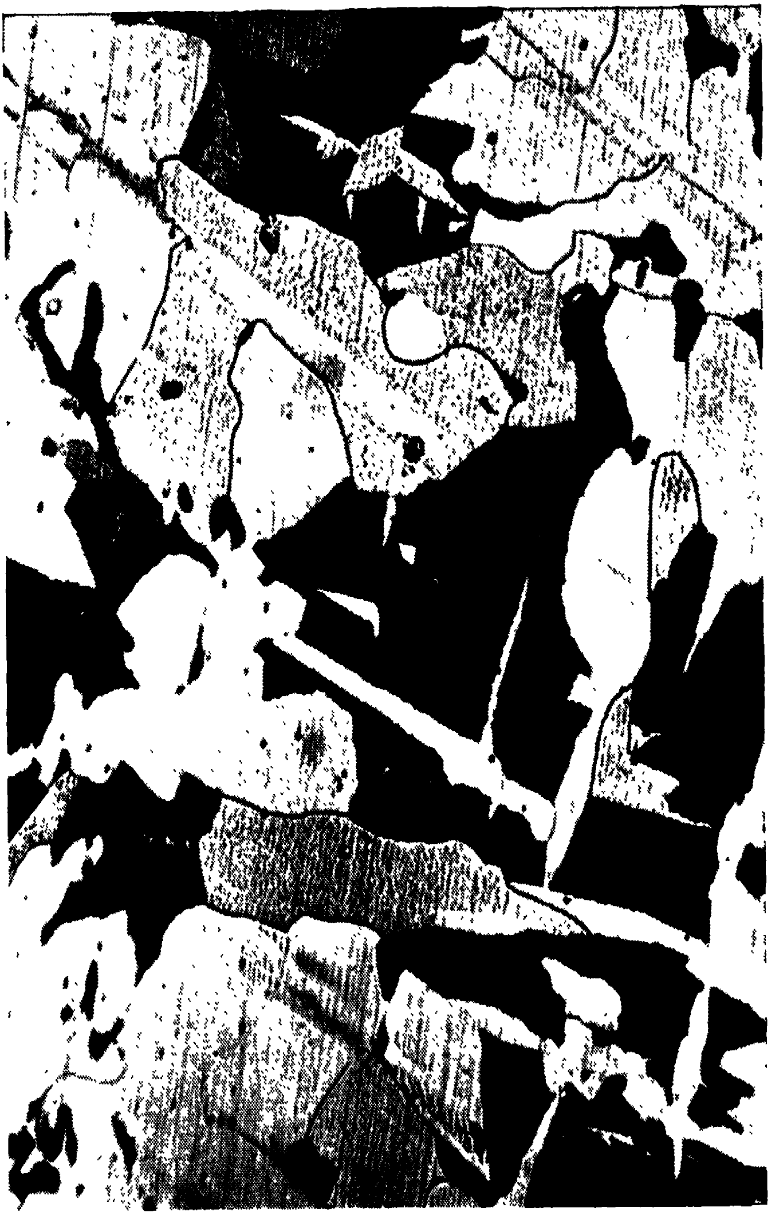


FIG. 162.—Microstructure of large mild steel forging.

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The influence of alloying elements, particularly chromium, is apparent in the restricted decarbonisation and absence of selective fissuring in the higher chromium steels. Similar results were obtained by Campbell, Ross and Fink (*J. Iron and Steel Inst.*, 1923, **108**, No. 11, page 173, and C. R. Austin (*J. Iron and Steel Inst.*, 1922, **105**, No. 1, 93).

Jaques (*Comptes Rendus*, 1932, 878-880) has carried out some interesting experiments on the effect of hydrogen upon the walls of steel vessels when subjected to an internal hydrogen pressure of 150 atms. and a temperature of 400-700° C. He found that the rate of decarbonising was influenced greatly by temperature. Four identical specimens were submitted to the same hydrogen pressure, viz. 150 atms., but at temperatures of 500, 550, 600 and 650° C., for two hours. The two specimens at the lower temperatures did not appear to be affected, but the two at the higher temperatures were decarbonised to a slight but perceptible depth. Jaques concludes from his experiments that temperature plays a more important part than pressure, that the chemical constitution and heat treatment of the steel are very important, and that cold drawn or other steels left in an initial state of stress, are most susceptible to this trouble.

The subject of the attack of steel by hydrogen has naturally received the attention of the large chemical manufacturing organisations, and I am indebted to Imperial Chemical Industries Ltd., for the following résumé of their experience in this connection.

It has been found that the variables which influence the attack of steels by hydrogen are as follows :—

(*a*) Pressure.
(*b*) Temperature.
(*c*) Stress.
(*d*) Composition of steel.
(*e*) Heat treatment of steel.

Thus it has been found that for any given steel under given pressure and stress conditions, the limiting temperature causing attack will depend upon the structural condition of the steel, i.e. upon the heat treatment. As an example, the case may be taken of a large mild steel forging in the normalised condition having a microstructure, of which Fig. 162 is typical, i.e. a structure consisting of massive pearlite and ferrite. Such a vessel under a pressure of hydrogen of 250 atms. will be attacked at temperatures as low as 200° C. If the same steel could be heat-treated to give a fine grained structure—preferably sorbitic pearlite and ferrite—hydrogen attack would not occur at this or even at a somewhat higher temperature.

The mechanism of hydrogen attack is now fairly well understood, at all events for all practical purposes. In the first stage of the attack the steel absorbs hydrogen, and this causes embrittlement, even though no decarburisation or disintegration has occurred. Means have been devised for measuring this amount of absorbed hydrogen, and in some cases it has been found that the steel has absorbed five times its own volume of hydrogen prior to any visible effect. The effect of this absorption is to reduce the izod impact value and bend value considerably and also to reduce the proportional limit. At this stage, the steel can be restored to its original state of ductility by a simple heat treatment which will drive off the absorbed hydrogen. After this absorption stage the steel becomes decarburised and fissured and this stage of attack is best illustrated by Figs. 163, 164 and 165, which show this attack in the case of mild steel and nickel-chromium-molybdenum steel respectively. Naturally, the strength of vessels in which the wall material has reached such a stage as is shown in Figs. 164-165 is extremely low, and such vessels would be in a most dangerous condition.

It has been stated that the critical conditions giving rise to attack depend upon the structural condition and, generally speaking, a fine complex structure is desired. In most cases, therefore, the hardened and tempered condition would be more suitable, although it should be noted that with thick sections the structural condition desired can rarely be obtained, even with careful heat treatment. Further, even if the ideal structural condition is obtained, the composition of the steel still imposes limitations on the conditions for safe use. Thus, even in the ideal structural condition nickel-chromium steel (3 per cent. Ni, 1 per cent. Cr) is insufficiently resistant under 250 atms. pressure and, say, 400° C. Investigation has shown that the generally used engineering alloy steels such as Ni-Cr, Ni-Cr-Mo, Cr-V, etc., are superior to mild steel, and tubes and small forgings in these steels can be safely used under conditions which would result in comparatively rapid failure with mild steel. These steels are, however, insufficiently resistant to many of the more exacting conditions which have to be met in present-day high-pressure technique. Investigation has shown that the addition of chromium to steel progressively improves its resistance to hydrogen attack. Thus, a steel containing 3 per cent. chromium has been found to be more resistant to attack than the alloy steels just mentioned, although it was appreciably attacked after a year at 450° C. Steels containing 5-6 per cent. chromium appear to be better suited to the more strenuous conditions, while valve steel (8 per cent. Cr, 3 per cent. Si) and stainless steel (12-14 per cent. Cr) are alternatives.

The chromium-nickel austenitic steels are not disintegrated by hydrogen at 250 atms. and temperatures up to 500° C., but they suffer considerable embrittlement due to the large amount of hydrogen which they absorb. On the grounds of this large hydrogen

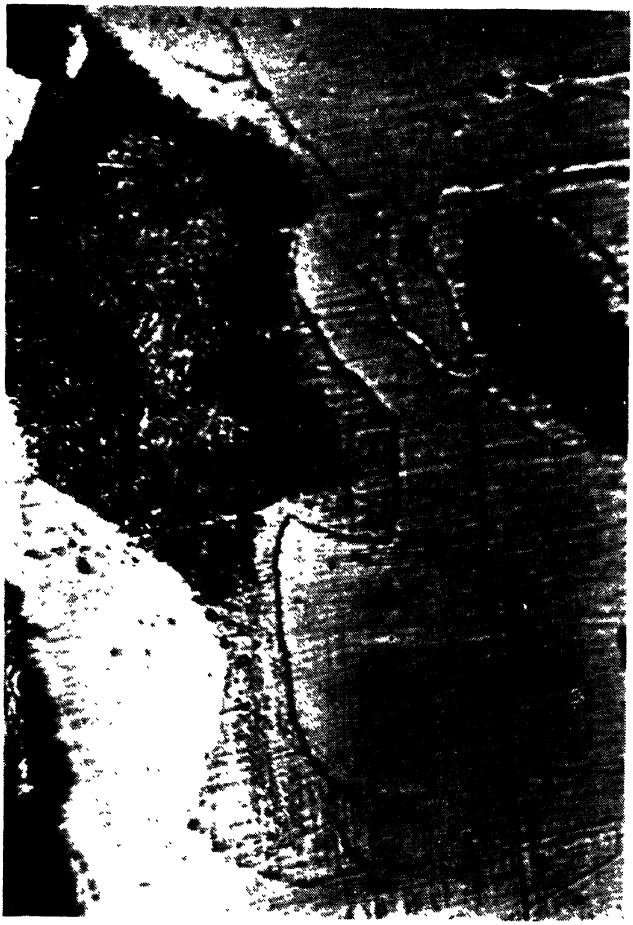

Fig. 163.—Showing partially decarburised pearlite area in a large mild steel forging after being subjected to hydrogen at 200 atms. and a temperature of about 250° C.

[*To face page* 248.

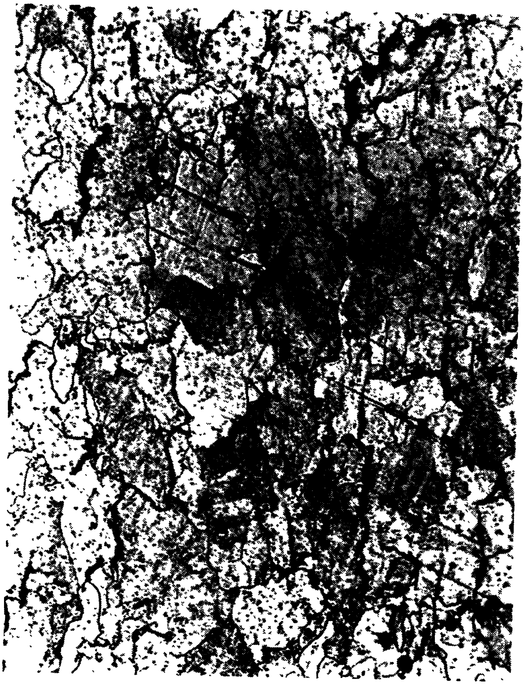

FIG. 164.—Completely decarburised and fissured mild steel after a few weeks under hydrogen at 250 atms. and 450° C.

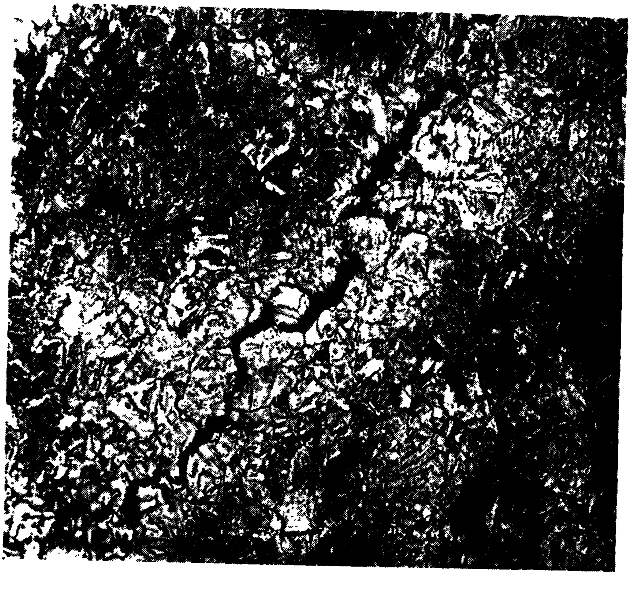

FIG. 165.—Ni-Cr-Mo steel decarburisation and fissuring due to hydrogen attack.

[*See page* 248.

absorption and necessary expense, this class of steel is not recommended for resistance to hydrogen attack, unless other corrosive media are present in addition to hydrogen.

Inglis and Andrews of Imperial Chemical Industries Ltd., have recently published some results in connection with hydrogen attack on steels. (Advance copy *Proc. Iron and Steel Institute*, September, 1933.)

The method of test was as follows :—

Pure hydrogen was passed at the required pressure through tubes of the steel under test, these tubes being heated to the requisite temperature, either by enclosing them in an electric furnace, or else in a steam jacket (the latter method was employed for temperatures below 300° C. and the former for temperatures above 300° C.). In some cases the hydrogen was passed through the tube in a continuous stream ; in other tests the tube was fitted with a blank flange at one end, filled with hydrogen under pressure, and the valve to the compressor then closed so that the tube was filled with stagnant hydrogen under pressure. In these latter cases, however, the tube was frequently refilled with fresh hydrogen (about every two days). The tubes were continuously under the test conditions, there being no shut-downs at nights or at week-ends. For most of the time the pressure was within ± 5 atms. of the stated pressure, whilst the maximum variation was ± 10 atms. Similarly, the temperatures in all cases were, for almost all the time of tests, within ± 5° C. of the required temperature, with a maximum variation of ± 10° C.

After a period under these test conditions, each tube was removed from its furnace and a small sample ring cut from it for examination, after which the joints were re-made and the tube was put back under test for a further period. The tubes were all purchased in the open market, and are entirely representative of normal production in their respective compositions. In most cases final heat treatment was carried out by the authors, since it was necessary to test the material in various structural conditions. The tubes were of different sizes, but in all cases the inside diameter was within the range 1¼ to 2 ins. ; the wall thickness was naturally chosen to give the desired stress under the test pressure.

MATERIALS TESTED.

The compositions of the various steels tested are given in Table 17. Steels 3-7 were all tested in the hardened and tempered condition, in such a condition as to give the optimum combination of strength and toughness. The mild steels were tested in different conditions of heat treatment, as will be apparent later.

TABLE 17.

	Mild Steel.		Ni-Cr-Mo Steel.	Cr-V Steel.	3% Cr Steel.	Cr-Si Steel.	6% Cr Steel.
Steel No.	1.	2.	3.	4.	5.	6.	7.
	%	%	%	%	%	%	%
Carbon . . .	0·12	0·12	0·28	0·40	0·33	0·58	0·18
Chromium . .	nil.	nil.	0·70	1·20	3·01	8·36	6·35
Nickel . . .	nil.	nil.	3·38	0·08	nil.	nil.	nil.
Molybdenum . .	nil.	nil.	0·38	nil.	nil.	nil.	nil.
Vanadium . .	nil.	nil.	nil.	0·30	nil.	nil.	nil.
Silicon . . .	0·07	0·01	0·21	0·17	0·12	2·50	1·28

The conclusions from these specific experiments have been completely checked and confirmed by the examination of various plant parts removed from service after periods under high-pressure and high-temperature conditions.

The conclusions reached are briefly as follows :—

(1) At high pressures hydrogen will attack steel at much lower temperatures than those causing attack at normal pressure.

(2) In the first stage of the attack the steel absorbs hydrogen, and this will cause embrittlement even though no decarburisation or disintegration has occurred. At this stage the steel can be restored to its original state of ductility by a suitable heat treatment to drive off the hydrogen. In the later stages of attack the steel becomes decarburised and fissured, with consequent very severe loss in strength and ductility.

(3) The factors which determine the degree of attack are as follows :—

(*a*) The temperature.
(*b*) The pressure.
(*c*) The stress.
(*d*) The composition of the steel.
(*e*) The structure of the steel.

(4) In any one steel the critical conditions giving rise to attack vary according to the structural condition of the steel, that is, according to the heat treatment. For any one steel, the best structural condition is one in which the grain-size is small, and, in general, the hardened and tempered condition is recommended.

(5) The limiting temperature giving rise to attack on mild steel may vary from 50° to 100° C., depending upon the precise structural condition. A large thick-walled vessel, in which the desirable structural condition cannot be attained, may be attacked at tem-

peratures as low as 200° C., but smaller vessels in the same composition can be heat-treated to give satisfactory resistance at 200° C.

(6) The generally used engineering alloy steels, such as nickel-chrome, nickel - chromium - molybdenum, chromium - vanadium, chromium-molybdenum steel, etc., have superior resistance to mild steel. The difference in structure between large and small vessels, after heat treatment, is much less than with mild steels, since these alloys are more responsive to heat treatment. In the properly heat-treated condition, the limiting temperature causing attack of these steels at 250 atms. is between 300° and 350° C.

(7) In connection with the limiting temperatures causing attack, the effect of variations in the structure throughout any one tube or vessel must be appreciated. For example, it has been found that even a light sealing weld may alter the structural condition of the steel in the immediate neighbourhood of the weld to such an extent that attack will occur there under conditions which do not cause attack of the remainder of the steel. It is necessary, therefore, to heat-treat such parts after welding.

(8) It has been shown that additions of chromium to steel progressively improve the resistance to hydrogen attack. Thus a 3 per cent. chromium steel is resistant, to 250 atms. up to 400° C., but is appreciably attacked at 450° C. On the other hand, a 6 per cent. chromium steel is resistant up to 500° C., at least.

(9) Chromium-nickel austenitic steels are not disintegrated by hydrogen at 250 atms. and temperatures up to 450° C., but these steels absorb large quantities of hydrogen under these conditions and consequently suffer severe embrittlement. The ductility can be restored by heat treatment to expel the absorbed hydrogen. They also undergo the familiar " boundary carbide " precipitation under these conditions.

In the recent paper * by Cox, to which reference was made in the section of this chapter devoted to creep, there are some interesting notes on hydrogen attack of steels. Cox states that at 500° C., and atmospheric pressure, high carbon steel suffered no decarburisation in molecular hydrogen in an exposure of one week. At the same temperature and 1250 lbs. per sq. in. the skin carbon of a 1·40 per cent. carbon steel was reduced to 1·10 per cent. in 16 hours.

In 16 hours at 500° C., with 3000 lbs. per sq. in. pressure, the surface carbon was reduced from 1·40 to 0·10 per cent. At ·04 in. from the surface the carbon was 0·20 per cent. Continuing the exposure to 48 hours reduced the carbon to that figure at a depth of ·052 in. The rate of attack falls off with decrease of carbon, a three-fold exposure increasing by only 30 per cent. the depth at

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* See page 224.

which the same carbon is found. Under the same conditions a strip of 0·05 per cent. carbon steel was completely decarburised in 168 hours.

At 700° C., and atmospheric pressure, ordinary mild steel is rapidly decarburised by molecular hydrogen and suffers intercrystalline injury. The rate of attack increases with the temperature. Cold working of the metal is also conducive of increased attack. Alloy steels are more resistant than carbon steels to hydrogen.

In a series of tests lasting 168 hours at 500° C., and 3000 lbs. per sq. in. of still hydrogen, "Nitralloy G," "N-4," and certain samples of "18 and 8" showed very slight decarburisation. The last alloy can be considered practically immune to hydrogen attack under these conditions. The compositions of these alloys are approximately as follows :—

	Nitralloy G.	N-4.	18 and 8.
C	0·30-0·40	0·23	0·12
Mn	0·30-0·60	0·45	0·50
Si	0·30	0·16	0·50
Cr	1·00-1·50	0·87	17-19·00
Ni	0·50	2·78	7-9·00
Mo	0·25	—	—
Al	1·25	—	—
Cu	—	0·12	—

Chrome-vanadium, chrome-vanadium-aluminium, chrome-nickel-vanadium-aluminium steels, stainless steel, 18 and 8 (chrome-nickel), 24 per cent. chrome-20 per cent. nickel, and BTG metal (12 per cent. chrome, 60 per cent. nickel with 2·5 per cent. tungsten), were completely resistant. In service the 24 per cent. chrome-20 per cent. nickel alloy has been exposed without failure for many thousands of hours to high-pressure hydrogen at temperatures as high as 440° C. BTG metal is regularly used at temperatures as high as 565° C. under pressure of 1000 atms. of hydrogen, with a fibre stress as high as 25,000 lbs./sq. in., and failure occurs after a life measured in thousands of hours, provision being made that failure shall not result in an accident.

Early in the development of its method for synthesising ammonia, the General Chemical Company tried a number of materials in the form of bottles filled with a nitrogen-hydrogen gas mixture and held at 1500 lbs./sq. in. and 500-600° C., until failure, with the following results, according to Wheeler :—

Material of Cylinder.					Time under Test before Failure.
Type of Steel.	C.	Ni.	Cr.	V.	
Plain carbon . .	0·35	—	—	—	4 months
Carbon chrome . .	1·06	—	0·65	—	4 months
Nickel . . .	0·43	3·59	—	—	6 months
Chrome-vanadium .	0·54	—	1·00	0·38	Over 2 years

The problem was studied by Wheeler at the Watertown Arsenal in 1917-18 on a wide range of ordinary and special steels, using 650° C., and atmospheric pressure. Because he did not use operating pressures, his results are not of quantitative value, but it is interesting to know that he found low carbon a necessity ; that the resistance of chromium steels increased with increasing chromium content but not in proportion to it ; that vanadium offered some resistance ; that titanium, tungsten and molybdenum in small quantities had an effect like chromium ; that manganese, silicon, nickel, aluminium, uranium, boron and zirconium had either no effect or were harmful ; that tungsten was the only pure metal tried that was not seriously affected.

Tungsten having made a good showing in earlier tests, a further series of seventeen steels was made by the Midvale Steel Company, with tungsten from 0·81 to 11·69 per cent. and chromium from zero to 2·49 per cent., together with a 2·42 per cent. chromium-0·20 per cent. vanadium, a plain 2·67 per cent. chromium and a 2·20 per cent. chromium-29·35 per cent. nickel analysis, which were exposed for a year to 10 per cent. ammonia in a $N_2 : 3H_2$ mixture at 300° C., and 600 atms.—a lower temperature and higher pressure than before. Tested for strength and hardness, but not microscopically, a preliminary report (not yet published) says that tungsten materially improved resistance up to 2·85 per cent., with no gain above it, and with lower results at 11·69 per cent. Chromium 1 per cent. proved better than tungsten 0·8 per cent., and, oddly, as good as 2·67 per cent. chromium under these conditions. The steel with

C	0·12 per cent.
Cr	1·01 „
W	3·10 „

after exposure, showed practically no change in its excellent properties of 72,000 lbs./sq. in. tensile strength, 34,000 lbs./sq. in.

yield point, 33 per cent. extension in 1½ in. and 55 per cent. reduction of area. Just as good was the showing of a heat with

C	0·35 per cent.
Cr	1·00 ,,
V	0·07 ,,

containing no tungsten.

Commercial copper, not deoxidised, after an exposure of over 1500 hours in the $N_2 : 3H_2$ mixture at approximately 550° C., and 1000 atms., has had its properties reduced from 30,700 lbs./sq. in. tensile strength, 65 per cent. elongation, 50 per cent. reduction of area to 25,040 lbs./sq. in. tensile strength, 20 per cent. elongation, 18 per cent. reduction of area. Under similar conditions phosphor bronze suffered no injury.

In 500 hours at the same exposure, Armco Iron was attacked at the grain boundaries, its tensile strength, elongation and reduction of area being reduced to zero. KA-2 alloy, the well-known 18 per cent. chromium-8 per cent. nickel steel, before the exposure gave 92,000 lbs./sq. in. tensile strength, 72 per cent. elongation and 63 per cent. reduction. After 162 hours in a 75 per cent. $H_2 : 25$ per cent. N_2 mixture at 500° C., and 1000 atms., its properties were 62,600 lbs./sq. in. tensile strength, 8 per cent. elongation, 18 per cent. reduction of area.

According to Saklatwalla * chrome-nickel steel was used abroad in catalyst chambers for ammonia synthesis, but recent plants are employing chrome-vanadium steel. According to Cox, in U.S.A. chrome-vanadium steel has been used exclusively, the exact proportions varying somewhat according to the size of the vessel, with the average composition running about 0·30 per cent. carbon, 2 per cent. chromium, 0·20 per cent. vanadium, usually normalised and tempered, the physical properties depending on the exact composition, treatment and section tested, ranging from 70,000 to 105,000 lbs./sq. in. tensile strength, 35,000 to 75,000 lbs./sq. in. proportional limit, 25 to 20 per cent. elongation in 2 ins. and from 55 to 40 per cent. reduction of area.

Accurate information from the field upon the behaviour of metal is usually considered confidential, because of the concern of chemical manufacturers for the preservation of their trade secrets, but Cox mentions a case where certain interior parts bought to the specification given below failed in one year in $N_2 : 3H_2$ at 550° C. and 300 atms., showing after exposure the composition range given in the second column :—

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* *Metals and Alloys*, 1929, **1**, 8-13.

	Specification.	*Range of Compositions after Exposure—showing Decarburisation.*
C	0·15-0·25	0·02-0·13
Mn	0·50-0·80	0·51-0·85
Cr	0·80-1·20	0·85-1·07
V	0·15-0·18	0·11-0·18
P	max. 0·04	
S	max. 0·04	

One sample showed loss of carbon from 0·22 to 0·03 per cent., and increase of nitrogen from 0·0042 to 0·132 per cent.

In some tests reported by Krupp (in a private communication to Cox), made in a hydrogen-nitrogen mixture at 450° C., and 300 atms. for 630 hours, Monel metal, after exposure, broke in the hand; copper lost three-quarters of its elastic limit, nearly half its extension, and three-fourths of its reduction of area; 18 per cent. chromium-8 per cent. nickel did much better, losing chiefly half its reduction of area; Sicromal, a very low carbon chrome-aluminium-vanadium-molybdenum steel, was hardly affected. Cox is not certain of the exact composition of this steel, but believes it to be approximately

C	0·06 max.
Mn	0·30
P	0·02 max.
S	0·02 max.
Si	0·40
Cr	5·00
Al	0·75
V	0·05
Mo	0·40

This composition would do well for interior parts, but could not be produced in the large masses required for the usual catalyst vessel.

Another composition, intended for destructive hydrogenation and other reactions with carbonaceous materials, contains

C	0·10
Cr	6·00
Mo	0·50

The BTG metal previously mentioned as being used for most exacting service in the synthesis of ammonia by the Claude process is adapted also for equipment used in the production of synthetic hydrocarbons. It cannot be produced in very large masses, nor can pieces of considerable size be forged. The Claude cylinders are made as solid castings bored out and heat-treated. Their life at a stress of approximately 25,000 lbs. per sq. in. at about 560° C., and 1000 atms., varies from about 2000 to nearly 20,000 hours, depending on the excellence of the individual part and the care exercised in its use.

Quite recently Messkin and Margolin (*Arch. Eisenhütten*, 1932-33, **6**, 399-405) have carried out an interesting series of experiments in connection with the effect on the magnetic properties of steel with 0·1 per cent. C and 4 per cent. Si of heating in hydrogen at temperatures up to 450° C., and under 1-615 atms. pressure. The removal of carbon and the reduction of dissolved and occluded oxides by the hydrogen increases the coercivity and reduces the watt losses, but the adsorption of hydrogen by the steel has the opposite effect. Part of the hydrogen disappears slowly from the steel at room temperature, but rapidly when the steel is heated to 100-150° C. The remainder of the hydrogen can only be removed by heating to 800° C., for four to six hours, preferably *in vacuo*. Only after removal of the hydrogen do its beneficial effects on the magnetic properties appear, but the steel then becomes very brittle owing to the small fissures produced by the escape of water, methane, etc., after the hydrogen treatment. These fissures reduce the permeability and electrical conductivity. Excellent magnetic properties without deterioration of the mechanical properties are produced by treating the molten steel with a blast of hydrogen which removes all oxygen, sulphur, phosphorus and carbon, and allowing the metal to cool slowly so that the excess of hydrogen escapes without producing pores. Such metal, owing to its coarse crystal structure, must be forged at 1180° C., and subsequently annealed at 825° C. for six hours. It then shows a coercivity of 0·33 Oersted with a watt loss of 1·01W/kg.

In the Claude process for the production of synthetic ammonia (1000 atms. and 500-550° C.), due to hydrogen attack, ordinary steels would fail in a few hours. A high nickel high chromium steel (57 per cent. Ni, 12 per cent. Cr, 1·7 tungsten) has given as much as 20,000 hours' service (*Nickel Bulletin*, 1931, **4**, page 328). In the synthesis of urea from ammonia and carbon dioxide (100 atms. and 150° C.) and under the corrosive action of a molten reaction mixture of urea, water and ammonium carbamate, successful results have been achieved with steels containing 58·5 per cent. Ni, 21·5 per cent. Cr and 1·4 per cent. Si. In oil refining extensive use is made of the 18 : 8 chromium nickel alloys, with additions of tungsten and molybdenum for special parts (*A.S.T.M. Symp.*, June, 1931, pp. 23-41).

In a recent English patent (389,887 of 1933) granted to Vereinigte Stahlwerke Aktien Gesellschaft of Dusseldorf, Germany, claims are made that by a special hydrogen seasoning process before the final rolling or forging operation, parts of high-pressure high-temperature plant subsequently used with hydrogen can be rendered practically immune from attack by that gas.

According to one example, seamless tubes, prior to final drawing, are exposed for some time to hydrogen or gases containing this gas, at elevated temperatures and pressures (e.g. 400° C., and 100 atms.), and then finished in the rolls. The action of this treatment consists partly in extensive decarbonisation of the steel, and still more of an intercrystalline attack by hydrogen, in such a way that the cementite and also foreign substances such as oxides, sulphides, phosphides and other non-metallic compounds are decomposed by the action of the high pressure. The subsequent annealing and forging is stated to eliminate the microscopic cavities and to transform the iron or steel into a condition in which it is resistant towards hydrogen.

Steel treated in this way, it is stated, is distinguished by high tenacity, resistance to ageing, resistance to alkalies, and is no longer attacked by hydrogen at elevated temperatures and pressures, even under long exposure thereto.

An example is as follows :—

> Tubes with a finished outside diameter of 120 mm. and an inside diameter of 82 mm. intended for the construction of high-pressure apparatus and composed of a steel containing 0·12 per cent. of carbon, 0·25 per cent. of silicon, 0·58 per cent. of manganese and less than 0·03 per cent. of sulphur and phosphorus, are treated in the following manner in rolling: When the internal diameter attains 70 mm., the rolling is interrupted and the scale on the outside and inside is removed by pickling or sand blasting. The tubes are then treated with technically pure hydrogen for twenty-four hours in a pressure chamber at 450° C., and a positive pressure of 150 atms., preferably with circulation of the hydrogen under pressure during the treatment, and with suitable condensation and removal of the water formed. At the end of about twenty-four hours, the pressure is relieved and the tubes are heated in a skid furnace to a temperature of from 1030 to 1070° C., in an excess of hydrogen, and then rolled to completion. The tube has the composition : C, 0·2 per cent. ; Si, 0·27 per cent. ; Mn, 0·58 per cent. ; P, 0·012 per cent. ; S, 0·009 per cent.

(*Author's Note.*—I think the carbon content of the tube after hydrogen treatment should be 0·02 per cent., and not 0·2 per cent. as stated in the original patent.)

Tubes treated in this manner display the following mechanical properties : Yield point 18 kgs. per sq. mm. Tensile strength 33 kgs. per sq. mm. Elongation 34 per cent. Reduction of area 72 per cent. The described treatment is stated to very greatly increase the resistance of the steel to the action of hydrogen under pressure, as is shown by the following test. Breaking-test pieces from a tube rolled to a finish under the usual conditions—and therefore not treated with hydrogen under pressure—and similar pieces from tubes treated in accordance with the invention, were exposed to the action of pure hydrogen in a pressure vessel at 450° C., and 100 atms. positive pressure, and tested to destruction after various durations of exposure.

The test pieces from the tube rolled in the usual way were found to be quite brittle after a treatment of twenty-four hours, whereas those treated in accordance with the invention retained their original tenacity after an exposure for 300 hours. This is shown by the following table :—

TABLE 18.

MECHANICAL PROPERTIES AFTER TREATMENT WITH HYDROGEN UNDER PRESSURE.

Material.	Duration of Treatment. Hours.	Yield Point. Kg./sq. mm.	Tensile Strength. Kg./sq. mm.	Elongation. Per Cent.	Reduction of Area. Per Cent.	Tenacity: Notched Bars. Mkg./sq. cm.
Ordinary tube	24	15	19	6	15	less than 1
Tubes treated in accordance with the present invention	24	18	33	33	71	above 20
	300	17	32	33	75	above 20

There is one final consideration in connection with high-pressure high-temperature plant, and that is the stress produced in the walls of the vessels by the difference in temperature between the inside and outside of the shell, caused by external or internal heating. This must be taken into account, and the alignment charts (Fig. 166) proposed by Barker (*Engineering*, 1927, 124, 443) are most useful in this respect. It will be noted that as $\frac{D}{d}$ increases the temperature difference stress also increases ; this also applies in the case of the factor $\frac{mE\alpha}{m-1}$,

where $m = 4\left(\frac{1}{m} = \text{Poisson's ratio}\right)$ for most steels.

E = Modulus of elasticity.

α = Coefficient of expansion of the material.

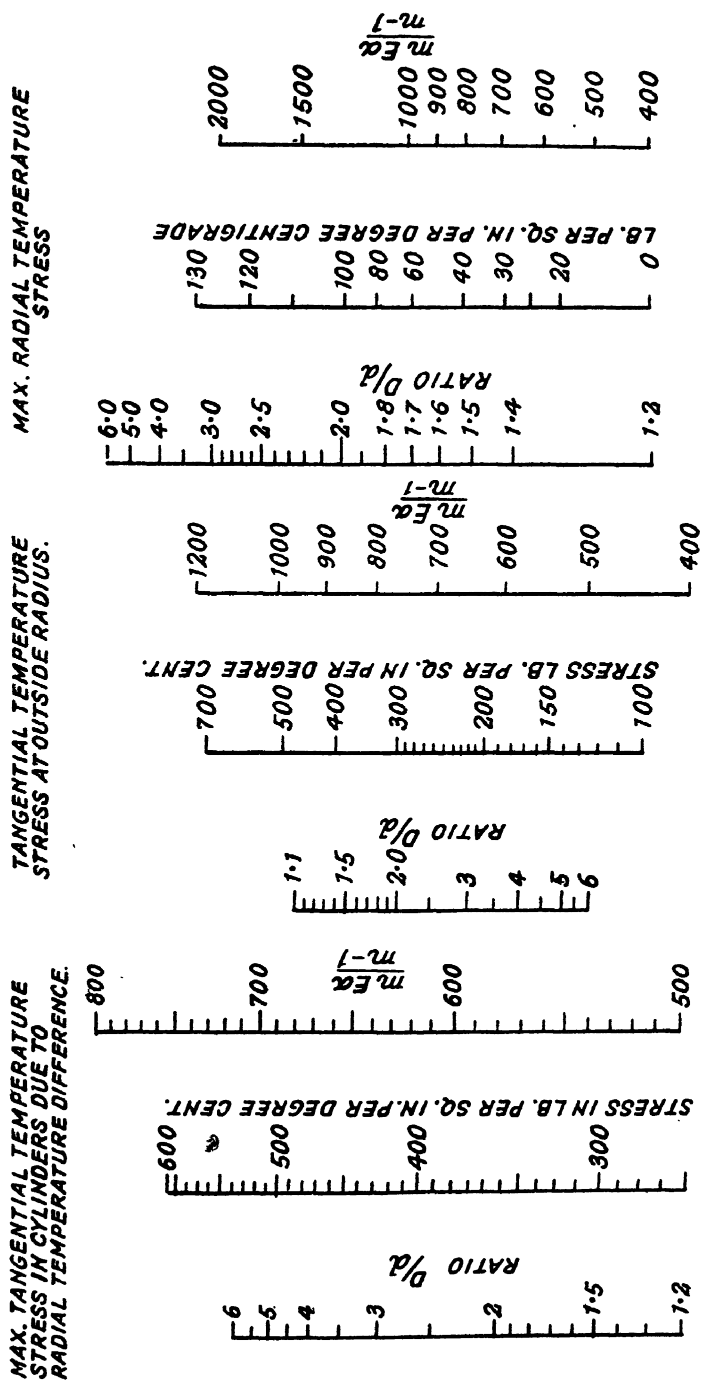

Fig. 166.—Alignment charts for temperature difference stress.

Both E and α vary with temperature, and Tables 19-20 give particulars of these variables.

TABLE 19.

VARIATION OF MODULUS OF ELASTICITY WITH TEMPERATURE OF CARBON STEELS.

Temperature °C.	E.
20	$30{\cdot}0 \times 10^6$
100	29·2
150	28·6
200	28·1
250	27·5
300	26·9
350	26·2
400	25·2
450	23·7
500	21·1

TABLE 20.

MEAN COEFFICIENT OF EXPANSION PER °C.

Range.	NiCrMo Steel. 2·5 Ni, 0·6 Cr, 0·6 Mo.	0·25 per Cent Carbon Steel.	"Staybrite" F.S.T. (Stainless Steel).	HR Crown (High Chromium-Nickel-Tungsten Heat-resisting Steel).
20—100° C.	·0000114	·0000115	·0000160	·0000152
20—200	·0000120	·0000121	·0000168	·0000156
20—300	·0000126	·0000128	·0000175	·0000159
20—400	·0000133	·0000134	·0000179	·0000162
20—500	·0000139	·0000139	·0000182	·0000165
20—600	·0000144	·0000144	·0000185	·0000168

Orrok (*Trans. Amer. Soc. Mech. Eng.*, 1927, **49**, 50) considers that up to 400° C., the alloy steels behave insofar as E is concerned exactly as the carbon steels. Higher than 400° C., however, alloy steel show less sudden decrease, until at 500° C. the value of "E" is 17 per cent. less than at room temperature.

For all steels at 400° C. the value of "E" will be taken throughout this book at 25×10^6, and the following values are for carbon and alloy steels at higher temperatures :—

CARBON STEELS.

425° C.	450° C.	475° C.	500° C.
$24{\cdot}3 \times 10^6$	$23{\cdot}7 \times 10^6$	$22{\cdot}0 \times 10^6$	$21{\cdot}1 \times 10^6$

ALLOY STEELS.

$24{\cdot}75 \times 10^6$	$24{\cdot}25 \times 10^6$	23×10^6	$22{\cdot}5 \times 10^6$

In the alignment charts (Fig. 166), the following table gives the signs of the stresses for external heating. For internal heating all the signs are changed :—

Stress.	Radius.	Signs.
Hoop or Tangential.	Inside.	Tension.
Hoop or Tangential.	Outside.	Compression.
Radial.	All radii.	Tension.

In the event of the value $\frac{mE\alpha}{m-1}$ for a material not being on the scale of the line charts, the stresses can still be obtained therefrom because they are directly proportional to $\frac{mE\alpha}{m-1}$, e.g. if the stress in a particular case of a material for which the value of $\frac{mE\alpha}{m-1} = 1500$ is required, it is necessary first to find the value of $\frac{mE\alpha}{m-1} = 500$, and then multiply by 3.

The value of $(T_1 - T_2)$ is most easily obtained from the heat transfer figures and the conductivity of the metal :—

$$(T_1 - T_2) = \frac{Q}{K} r_2 \log_e \frac{r_2}{r_1}$$

where Q = kg. cals./sq. in. of external surface per hour.
K = conductivity of metal.
r_1 and r^2 = internal and external radii of tube.

Summary.

To sum up, the special factors governing the design of vessels and components for high-temperature service are :—

(1) At elevated temperature ordinary mechanical tests of materials are useful only as a test of quality of material, and are quite insufficient as a base upon which to calculate permissible working stresses.

(2) The "creep" of materials must be considered, and for experimental work (particularly in cases involving the use of new alloys) the time yield as suggested by Hatfield serves a very useful purpose as a basis for fixing working stresses. In commercial processes where accumulated experience is not available, longer time creep tests are desirable to ensure that the material does not undergo structural change, which might affect its mechanical properties.

In cases where corrosive or gas penetrative conditions are not present, there are three types of steel for pressure vessels and fittings :—

(*a*) Where the working stress is low carbon steels are quite satisfactory at temperatures not exceeding 440-450° C. ; if the working stress is high, or where the saving of weight is a consideration, the low alloy steels such as nickel-chrome-molybdenum may be used.

(*b*) For the temperature range 450-525° C. alloy steels should be used. Suitable alloy steels include nickel-chrome-molybdenum (2·5 Ni, 0·6 Cr, 0·6 Mo), carbon molybdenum, chrome molybdenum, copper chrome molybdenum (Hadfields Ltd., Era 131).

(*c*) At temperatures higher than 525° C., it is advisable to use the highly alloyed austenitic steels, which have been specially developed for such purposes.

(3) Some types of steel become embrittled at high temperatures, and care should be taken to exclude these where shock may occur.

(4) Many otherwise suitable steels are not satisfactory for use with hydrogen at high temperature and pressure, and this point must be borne in mind. For temperatures up to 500° C. or so the 6·0 per cent. Cr, 0·5 per cent. Mo steel appears to be best in these circumstances where corrosion is not present. For corrosive cases 18 : 8 stainless steel with addition of titanium and molybdenum is frequently used.

Above 500° C. the only available material appears to be BTG. alloy as used by Claude.

(5) An additional stress (a temperature difference stress) must be acknowledged in the case of externally or internally heated vessels, and it is worthy of note that an excessively thick wall is not necessarily stronger than one of optimum thickness, since the temperature difference stress increases with increase of $\frac{D}{d}$.

Recent English Patents dealing with Special Steels for High Pressure Chemical Service.

The following English patents in connection with the use of special steels for high-temperature high-pressure chemical plant are selected to illustrate the trend of development.

385,781. *High Pressure and Reaction Vessels. Destructive Hydrogenation.*

Krupp, A.G. February, 1932.

A container or reaction vessel for use in carrying out chemical processes under high pressure and temperature, e.g. the hydrogenation of coal, etc., consists of at least two nested hollow cylinders interconnected by shrinkage, and having a layer of heat insulating material on its outer surface. The inner cylinder may consist of material resistant to chemical attack, e.g. steel alloys which contain 5-20 per cent. chromium and about 0-3·0 per cent. of molybdenum, and an outer cylinder of material having considerable strength at high temperatures ; for example, steel alloys which contain about 1-5 per cent. chromium and up to 3 per cent. molybdenum with or without up to 0·5 per cent. of vanadium or titanium.

The amount of shrinkage is so chosen that in service the inner cylinder experiences only a small mechanical stress insufficient to reduce its capacity for resisting chemical attack.

260,888.

I.G. Farbenindustrie, A.G. June, 1926.

In working with reducing gases in apparatus made of or lined with copper or its alloys, in order to prevent the diffusion of the gases through the walls of the apparatus (which diffusion is ascribed to the presence in copper or its alloys of small quantities of the oxides of copper and of the metal alloyed therewith and to the reduction of these oxides by the gases), the walls of the apparatus are protected from the direct contact of the reducing gases by a layer of gas which is non-reducing with respect to these oxides. For example, the apparatus may be provided with an inner wall of copper or its alloys so that a narrow space is formed between the inner and the outer walls through which space the non-reducing gas such as nitrogen or carbon dioxide is slowly passed, at a pressure the same as the reducing gases. This invention is applicable to apparatus for use in the synthetic manufacture of methyl alcohol.

247,217.

I.G. Farbenindustrie, A.G. February, 1925.

For processes in which carbon monoxide is present under pressure, the parts of the apparatus which are exposed to a temperature of 150° C., or over, are provided with an inner surface of a resistant metal or alloy and the gases are employed in a particularly dry state ; when not exposed to a temperature above 150° C. the apparatus may be made of iron.

The protection of parts of the apparatus at a temperature higher than 150° C. may be effected (as described in E.P. 231,285) by constructing the said parts of copper, silver, aluminium or their alloys, or special steels with substantial percentages of chromium, manganese, tungsten, molybdenum or vanadium, or making the said parts of iron or steel lined with the above-mentioned alloys.

The gases may be dried by means of desiccated calcium chloride, or, in the case of the production of methyl alcohol by catalytic interaction of carbon monoxide and hydrogen under pressure, by washing the gases with the product.

161,195. *Apparatus for synthesis of ammonia.*

L'Air Liquide. April, 1920.

In the synthesis of ammonia under conditions of high pressure, the development of stresses in the wall of the pressure tube due to the difference in temperature between the inside and outside layers of the wall is minimised by heat insulating the exterior wall, thereby maintaining a fairly uniform temperature throughout the thickness of the metal.

307,843. *Apparatus for reaction involving ammonia at high temperature.*

I.G. Farbenindustrie, A.G. March, 1928.

Apparatus for heating ammonia gas (or mixtures containing it) to temperatures exceeding 400° C., is constructed of a metal (with the exception of those of the iron group and metals melting below 400° C.), e.g. copper, silver, aluminium or magnesium or an alloy of two or more such metals, or of a metal or metals with other elements such as silicon. Alloys containing 10 per cent. of silicon and 90 per cent. of copper and alloys containing 2 per cent. of phosphorus and 98 per cent. of copper can be used for this purpose.

365,619. *Destructive hydrogenation—Chemical apparatus.*

I.G. Farbenindustrie, A.G. 1931.

Apparatus for treating distillable carbonaceous materials containing sulphur with hydrogen at elevated temperatures is constructed wholly or in part of a material stable to hydrogen, coated internally with a thin coating, preferably of less than 1 mm., of silicon or of a metallic substance stable to corrosion by sulphur. Suitable materials stable to hydrogen are alloy steels containing 1-6 per cent. of chromium, aluminium, tungsten, vanadium, cobalt, manganese or nickel; to these may be applied electrolytically, by fusion, or by spraying, a coating of molybdenum, tungsten, chromium, titanium, silicon, aluminium, silver, zinc, brass or alloys of zinc with iron, nickel or copper. The alloy steel wall may be supported by an outer pressure bearing wall. Examples of the construction of the apparatus are given.

366,762. *Chemical apparatus—Destructive hydrogenation.*

I.G. Farbenindustrie, A.G. March, 1931.

Apparatus for carrying out reactions at elevated temperatures in presence of hydrogen is made of (or lined with) an alloy containing titanium, iron and aluminium and optionally also one or more of the elements chromium, tungsten, molybdenum, vanadium, silicon, nickel, cobalt, manganese, tin, zinc, lead, silver and beryllium. Specified alloys are:

(1) Fe 92·5 per cent., aluminium 6 per cent., titanium 1·5 per cent.

(2) Fe 91 per cent., aluminium 5 per cent., chromium 3 per cent., titanium 1 per cent.

361,856. *Chemical apparatus for destructive hydrogenation.*

Alloys. I.G. Farbenindustrie, A.G. 1930.

Apparatus for destructive hydrogenation and other reactions with carbonaceous materials in the presence of hydrogen is constructed of or coated with an iron alloy practically free from nickel and containing substituted amounts of chromium and molybdenum. The chromium content may be 3-18 per cent.; tungsten, vanadium, cobalt, aluminium or manganese may also be included in the alloy. The figure shows an apparatus comprising a preheating coil, a high-pressure reaction vessel containing a catalyst of molybdic acid and zinc oxide, and condenser. The preheater, the connecting pipes and the lining of the reaction vessel are composed of a steel containing 6 per cent. chromium, 0·5 per cent. molybdenum, 0·3 per cent. vanadium, 0·1 per cent. carbon, the remainder being iron.

PART II.

Materials for Service in High Pressure Plant when Exposed to Low Temperatures.

Apart from the properties of materials at high temperature, many cases occur in high-pressure work where a knowledge of the properties of stressed materials at low temperatures is essential. An example is the cold section of the plant in cases such as liquid air apparatus ; another is the portion of the plant maintained at low temperatures in the production of hydrogen by successive liquefaction of the other constituents of coke oven or water gas.

Whereas in the case of materials at high temperature, the tensile strength of practically all materials is considerably reduced as the temperature rises, at low temperatures the tensile strength is considerably increased. The chief difficulty at low temperature appears to be embrittlement.

The mechanical properties of materials at low temperatures have not been studied so extensively as those at high temperatures. The available literature of the subject has recently been described by Russell (*Am. Soc. Test. Materials and Am. Soc. Mech. Eng.*, p. 486, Sept., 1931). One of the most interesting of the early papers is that by Hadfield (*J. Iron and Steel Inst.*, 1905, **67**, 147), who tested a wide range of materials in liquid air and found that (particularly in the case of ferrous metals) materials became harder and more brittle as the temperature falls. High percentages of nickel and manganese, however, were found to check this tendency.

Guillet and Cornot (*Comptes Rendus*, 1922, **174**, 384) described the results obtained from a large number of experiments on the hardness and shock-resisting qualities of many metals and alloys at various temperatures down to that of liquid air. With low carbon steels they found that the impact value (or resistance to shock) fell rapidly with fall of temperature until at the temperature of liquid air the values were less than one-tenth those obtained at air temperature ; 30 per cent. of nickel reduced this diminution in impact value while pure nickel lost but a trifling amount of its value at ordinary temperature.

F. Pester (*Z. fur Metalkunde*, 1932, **24**, 67 and 115) found but little change in two of the mechanical properties (elongation and reduction of area) of drawn steel wire at temperatures down to − 60° C.

Cunningham and Gilchrist found that carbon steels show a gradual decrease in the impact value down to − 29° C., but that dead mild steels show little change in this respect down to − 40° C. (*Trans. Amer. Soc. Steel Treat.*, 1932, **9**, 624).

TABLE 21.

ANALYSIS OF MATERIALS USED.

Material.	Source of Supply.	Mark.	C, per cent.	Si, per cent.	S, per cent.	P, per cent.	Mn, per cent.	Ni, per cent.	Cr, per cent.
Armco iron . .	Commercial . .	A	0·035	Trace	0·016	0·003	0·02	—	—
Low carbon steel .	” . .	L	0·13	0·17	0·040	0·042	0·68	—	—
NiCrMo steel * .	” . .	V	0·33	0·16	0·012	0·035	0·64	2·54	0·67
NiCr steel . .	” . .	AN	0·17	—	—	—	—	10·1	15·8
” ” † . .	H.F. induction furnace	X 91	0·11	—	—	—	—	10·5	15·6
” ” . .	” ”	X 95	0·11	—	—	—	—	11·5	16·2
NiCrMn steel . .	” ”	X 96	0·06	—	—	—	4·07	10·05	13·45
” ” . .	” ”	X 92	0·43	—	—	—	3·65	10·2	13·8
NiCr steel . .	” ”	X 98	0·11	0·22	0·019	0·005	0·52	9·90	13·70
” ” . .	” ”	X 99	0·11	0·25	0·019	0·005	0·49	10·05	18·3
” ” . .	” ”	X 100	0·11	—	—	—	—	12·0	12·67
” ” . .	” ”	X 101	0·11	—	—	—	—	12·0	14·7
” ” . .	” ”	X 102	0·11	—	—	—	—	13·8	12·2
” ” . .	” ”	X 103	0·11	—	—	—	—	14·0	14·15
” ” . .	” ”	X 104	0·11	—	—	—	—	15·92	12·25

* Contains 0·64 per cent. molybdenum.

† Contains 0·25 per cent. vanadium and a trace of titanium.

Since all the melts in the high frequency induction furnace were made from the same raw materials it was only considered necessary to analyse two of the casts for silicon, sulphur, phosphorus and manganese.

Some very interesting results in connection with the properties of austenitic chrome-nickel steels at low temperatures have been recently given by Colbeck, McGillivray and Manning (paper read before Inst. of Chemical Engineers, 24th May, 1933), and I am indebted to the Institution for permission to publish this matter from the advance proof.

Table 21 (p. 267) shows the chemical analysis of the materials tested, and their source. The Armco iron, low carbon steel, and nickel-chrome-molybdenum steel were included for control, and purposes of comparison.

The tests carried out were ordinary tensile and impact tests. In the latter case, the standard Avery 120 ft.-lbs. machine was used, and specimens were quickly transferred from the cooling bath to the vice grips of the machine to avoid sensible temperature rise. The whole operation did not take more than seven seconds, and the authors found that in such circumstances the error was negligible.

The tensile tests were carried out in a simple hydraulic testing machine, and a cryostat surrounded the test specimen. A special extensometer of the tilting mirror type was fitted.

The tensile test results are given in Table 22.

The Izod impact test results are given in Table 23.

TABLE 22.

TENSILE RESULTS.

* Average of 2 Tests.

Material.	Diam. of Test piece in ins.	Temp. of Test. °C.	Ult. Strength. Tons/sq. in.	Yield Point. Tons/sq. in.	Elongation. Per Cent. on 2 in.	Reduction of Area. Per Cent.	Fracture.	Analysis. Per Cent.
Nickel-chrome-molybdenum steel :	0·25	Room	68·0	61·5	14·0	65·0	Fibrous, radial ridges.	
	0·25	−21	69·0	62·9	15·6	64·0	Fibrous.	
	0·25	−60	73·2	64·0	14·0	63·0	Jagged edges.	Carbon . 0·33
	0·25	−67	72·8	65·0	15·6	62·0	Very jagged edges, radial ridges.	Nickel . 2·45
Oil hardened 850° C.	0·25	−96	76·1	66·6	16·4	61·0	Jagged edges, longitudinal split.	Chromium 0·67
	0·25	—180	90·0	82·0	17·0	63·0	Jagged edges.	Molybdenum 0·64
Tempered 640° C.	0·504	Room	72·6	66·2	19·0	61·0	Fibrous, radial ridges.	
	0·504	−180	93·0	88·5	20·0	50·0	Broke in four pieces.	
Armco iron as received.	0·25	Room	20·4	N.O.	27·9	73·2	Fibrous, silky.	*
	0·25	−20	24·0	13·7	42·0	75·0	Fibrous.	
	0·25	−50	26·5	18·8	43·0	74·0	Fibrous.	
	0·25	−70	27·5	19·4	37·5	72·0	Fibrous.	
	0·25	−100	29·8	25·5	26·5	70·0	Fibrous.	
	0·25	−120	34·4	29·8	17·0	68·0	Crystalline, fibrous core.	
	0·25	−180	50·0	N.O.	Nil	Nil	Coarsely crystalline.	
	0·504	Room	20·8	10·0	43·0	72·0	Fibrous, part cup and cone.	
	0·504	−180	49·7	N.O.	Nil	Nil	Coarsely crystalline.	
Low carbon steel as received —fine grain size, pearlite and ferrite structure.	0·25	Room.	29·6	24·4	29·7	71·8	Cup and cone.	
	0·25	−65	36·0	30·2	33·6	70·3	Part cup and cone.	Carbon . 0·13
	0·25	−180	54·2	N.O.	26·5	55·0	Crystalline.	Manganese 0·68
	0·504	Room	29·6	25·0	37·5	69·0	Fibrous, silky.	
	0·504	−180	54·2	50·7	27·0	32·5	Crystalline.	
X 98. Water quenched 1100° C.	0·25	Room	45·0	14·0	51·6	71·0	Jagged edges.	
	0·25	−20·5	64·4	17·2	44·5	75·0	¾ cup and cone.	
	0·25	−61·5	80·0	21·0	37·5	66·0	Part cup and cone, jagged edges.	Carbon . 0·11
	0·25	−101	86·3	15·8	25·5	63·0	½ cup and cone.	Nickel . 10·0
	0·25	−125	93·8	18·0	30·5	62·0	½ cup and cone.	Chromium 14·7
	0·25	−180	114·0	22·2	23·5	50·0	¾ cup and cone.	
	0·504	Room	45·0	16·7	58·5	72·3	45° shear, central cup and cone.	
	0·504	−180	190·5	29·4	28·0	49·0	Complete cup and cone.	

Material.	Diam. of Test piece in ins.	Temp. of Test. °C.	Ult. Strength. Tons/sq. in.	Yield Point. Tons/sq. in.	Elongation. Per Cent. on 2 in.	Reduction of Area. Per Cent.	Fracture.	Analysis. Per Cent.
X 99. Water quenched 1100° C.	0·25	Room	41·4	16·5	54·0	74·0	Jagged.	
	0·25	−20	51·0	19·0	62·5	73·0	45° shear, fibrous.	
	0·25	−60	61·1	22·2	61·0	74·0	½ cup and cone.	Carbon . 0·11
	0·25	−96	69·0	24·0	46·1	70·0	½ cup and cone.	Nickel . 10·05
	0·25	−116	80·0	32·5	48·5	63·0	¾ cup and cone.	Chromium 18·3
	0·25	−180	99·5	33·3	45·7	55·0	Part cup and cone.	
	0·504	Room	39·8	21·4	58·5	73·0	45° shear, small central cup and cone.	
	0·504	−180	87·0	43·7	42·0	61·0	Almost complete cup and cone.	
X 100. Water quenched 1100° C.	0·25	Room	37·0	15·2	58·0	77·0	½ cup and cone.	
	0·25	−21	47·3	15·0	64·0	76·0	Jagged edges.	
	0·25	−59·5	59·3	24·0	50·0	72·0	¾ cup and cone.	
	0·25	−98	74·5	15·0	43·0	67·0	Complete cup and cone.	Carbon . 0·11
	0·25	−120·5	81·2	19·4	38·0	64·0	Complete cup and cone.	Nickel . 12·0
	0·25	−180	105·0	28·2	36·0	50·0	Almost complete cup and cone.	Chromium 12·7
	0·504	Room	34·0	14·9	62·5	78·0	45° shear, small central cup and cone, jagged edges.	
	0·504	−180	101·9	35·8	37·0	53·0	Complete cup and cone.	
X 101. Water quenched 1100° C.	0·25	Room	38·8	11·0	50·0	74·0	Two 45° shears, V-notch.	
	0·25	−22	46·0	20·0	61·5	79·0	Cup and cone, jagged edges.	
	0·25	−61	56·1	24·0	61·0	76·0	½ cup and cone.	Carbon . 0·11
	0·25	−100	66·5	25·0	48·5	70·0	Complete cup and cone.	Nickel . 12·0
	0·25	−121	74·0	28·2	46·1	70·0	½ cup and cone, jagged edges.	Chromium 14·7
	0·25	−180	97·0	32·5	44·0	55·0	½ cup and cone.	
	0·504	Room	35·4	10·0	60·0	75·0	45° shear, small central cup and cone.	
	0·504	−180	94·7	35·75	45·5	55·0	Part cup and cone.	
X 102. Water quenched 1100° C.	0·25	Room	38·0	12·1	51·5	76·0	45° shear.	
	0·25	−20	42·0	15·0	67·0	80·0	½ cup and cone, jagged edges.	
	0·25	−62	47·5	20·8	60·0	78·0	Part cup and cone.	Carbon . 0·11
	0·25	−100	59·5	22·0	56·0	75·0	¾ cup and cone.	Nickel . 13·8
	0·25	−177	94·5	32·0	44·5	58·0	Complete cup and cone.	Chromium 12·2
	0·504	Room	34·7	14·65	57·0	75·0	Part cup and cone, central core.	
	0·25	−121	69·0	24·0	50·0	71·0	½ cup and cone.	
	0·504	−180	92·3	36·6	47·5	59·0	Complete cup and cone.	

X 103. Water quenched 1100° C.	0·25	Room	38·5	15·3	51·0	76·0	Fibrous, jagged edges.	Carbon . 0·11 Nickel . 14·0 Chromium 14·15
	0·25	−20	43·5	18·5	62·0	79·0	45° tear, central cup.	
	0·25	−61·0	50·0	19·4	70·3	76·0	45° tear, central cup.	
	0·25	−100	54·9	24·4	54·7	73·0	½ cup and cone.	
	0·25	−121	62·0	26·8	56·0	72·0	Part cup and cone.	
	0·25	−180	86·4	32·5	51·5	60·0	¾ cup and cone.	
	0·504	Room	35·6	15·0	52·3	75·0	½ cup and cone, central core.	
	0·504	−180	84·05	43·30	53·0	58·0	Part cup and cone.	
X 104. Water quenched 1100° C.	0·25	Room	37·2	14·5	44·5	78·0	45° tear, central cup.	Carbon . 0·11 Nickel . 15·92 Chromium 12·25
	0·25	−20·5	40·0	16·2	61·0	79·0	45° tear, central cup.	
	0·25	−62·0	45·0	17·2	61·5	77·0	45° tear, very small central cup.	
	0·25	−102	51·8	21·5	66·5	74·0	45° tear, central cup.	
	0·25	−121	55·5	24·5	69·0	73·0	¾ cup and cone.	
	0·25	−180	79·0	32·0	58·1	65·0	Part cup and cone.	
	0·504	Room	34·4	16·5	56·0	75·0	½ cup and cone, central core.	
	0·504	−180	77·20	37·2	64·0	67·0	Nearly complete cup and cone.	
X 95. Water quenched 1100° C.	0·25	Room	41·8	20·0	47·8	51·7	Fibrous, jagged edges.	Carbon . 0·11 Nickel . 11·5 Chromium 16·2
	0·25	−180	98·0	52·5	54·7	75·2		
	0·504	−70	57·3	34·6	65·0	75·0	½ cup and cone.	
	0·504	−180	94·0	50·0	50·0	64·0	Complete cup and cone.	
X 96. Water quenched 1100° C.	0·504	Room	35·9	17·2	59·5	75·5	45° shear, central cup and cone.	Carbon . 0·06 Nickel . 10·05 Chromium 13·45 Manganese 4·07
	0·504	−180	88·2	40·0	47·0	60·0	Part cup and cone.	
X 92. Water quenched 1100° C.	0·504	Room	50·0	24·0	43·0	47·5	Jagged, dusty.	Carbon . 0·45 Nickel . 10·2 Chromium 13·8 Manganese 3·65
		−180	76·9	63·8	14·0	14·0	Fibrous.	
X 91. Water quenched 1100° C.	0·504	−180	103·7	34·4	30·5	45·0	¾ cup and cone.	Carbon . 0·11 Nickel . 10·5 Chromium 15·6
Brown Bayley's "Anka" (as received).	0·504	−180	109·3	37·5	38·0	52·0	Almost complete cup and cone. 3 longitudinal splits.	Carbon . 0·11 Nickel . 10·1 Chromium 15·8

TABLE 23.

IZOD IMPACT TESTS.

Material.	Room Temp.	− 65° C.	− 120° C.	− 180° C.	Time of soaking in Liquid Air. In hours.	Impact after soaking in Liquid Air.	After warming up to Room Temperature.	Remarks.
Low carbon steel .	94·0*u*	99·0*u*	—	3·0*b*	—	—	91·0*u**	* After warming up under cold water tap from −65° C.
B. & B. " Anka "	—	—	—	75·0*u*	20	64·0*b*	—	—
†Vibrac . .	57·5*b*	53*b* (−74° C.)	50·0*b* 51·0*b*	22·0*b*	—	—	60·0*b*	—
Armco . .	78·0*b*	4*b* (−74° C.)	—	1·5*b*	—	—	83·0*u*	—
X 91 . .	113·0*u*	—	—	86·0*u*	350	70·0*u*	117·0*u*	Several other tests after soaking in liquid air are recorded for this steel.
X 95 . .	118·0*u*	118·0*u*	—	117·5*u*	336	117·5*u*	108·0*u*	—
X 96 . .	117·0*u*	117·5*u*	—	117·5*u*	336	117·0*u*	—	—
X 92 . .	61·0*b*	—	—	14·0*b*	—	—	—	—
X 98 . .	116·0*u*	99·0*u*	86·0*u*	79·5*b*	168	79·0*b*	118·0*u*	—
X 99 . .	114·0*u*	117·5*u*	107·5*u*	100·0*u*	192	100·0*u*	117·0*u*	—
X 100 . .	118·0*u*	117·5*u*	98·5*u*	102·0*u*	216	95·0*u*	107·5*u*	—
X 101 . .	117·0*u*	117·5*u*	117·5*u*	98·0*u*	216	95·5*u*	109·0*u*	—
X 102 . .	111·0*u*	117·5*u*	117·0*u*	102·0*u*	168	103·0*u*	99·0*u*	—
X 103 . .	117·0*u*	117·5*u*	117·0*u*	116·0*u*	168	103·5*u*	110·5*u*	—
X 104 . .	115·0*u*	117·25*u*	117·5*u*	117·5*u*	168	117·5*u*	100·0*u*	—

b Indicates that the specimen was broken in the machine.
u Indicates that the specimen remained unbroken.
† This is a NiCrMo steel (0·25 C, 0·6 Cr, 2·5 Ni, 0·6 Mo).

Regarding the results, the following are especially worthy of note :—

(1) *Tensile Tests.*

(*a*) The very high tensile strength obtained with some of the special steels at — 180° C.

(*b*) The very low yield point obtained with the austenitic steels over the whole range of temperature.

(*c*) The very small proportional alteration found in all the tensile properties of the martensitic nickel-chrome-molybdenum steel.

(*d*) The absence of ductility and the approach of the yield point to the ultimate strength in Armco iron at the lower temperatures.

(2) *Impact Tests.*

(*a*) Armco iron becomes quite brittle at temperatures of — 37° C.

(*b*) Low carbon steel shows no reduction in impact value down to — 65° C., but at — 180° C. has no resistance to impact.

(*c*) The nickel-chrome-molybdenum steel (Vibrac) shows little alteration in impact value down to — 120° C., but this falls appreciably at temperatures of — 180° C.

(*d*) There appear to be three types of austenitic steel when classified in connection with the response to low temperature insofar as impact value is concerned.

Firstly, there is the class which show practically no change in impact value even after prolonged soaking in liquid air.

Secondly, those which show no immediate change when cooled to — 180° C., but show a falling off when held for a period at this low temperature.

Thirdly, those which show a reduced impact value at intermediate temperatures, some of which show a further deterioration when held for periods in liquid air.

Regarding the austenitic steels, the study of which was the primary object of these investigations, in all cases the tensile strength was progressively increased from room temperature down to — 180° C. At this low temperature the tensile strength and yield point were two and three times as great as at ordinary temperatures.

Tensile strengths as high as 110 tons/sq. in. were recorded at — 180° C.

The authors draw special attention to the powerful stabilising effect of manganese. For example, ingot X 96 is almost identical with ingot X 98, with the exception that the former contains 4 per cent. of manganese. This has been sufficient to ensure that ductility and resistance to impact have been preserved down to — 180° C.

Special attention is also drawn to the embrittling effect of carbon under low temperature conditions, and the authors recommend that the carbon content should be below the maximum solubility of carbon in austenite.

Colbeck and McGillivray have recently published results of mechanical tests of non-ferrous materials at low temperature (*Inst. Chem. Eng.*, Advance proof, Nov., 1933). Their results for copper, aluminium, nickel and brass are tabulated below. :—

Material.	Temp. °C.	Izod. Ft. Lbs.	Ult. Strength. Tons/sq. ins.	Proof Stress. Tons/sq. ins.
Copper	R.T.	43·0	14·0	3·82
	— 80	44·0	17·2	4·50
	— 180	50·0	22·7	5·12
Nickel	R.T.	89·0	29·25	10·98
	— 80	92·0	34·1	12·27
	— 180	98·5	43·7	12·47
Brass	R.T.	65·5	22·8	12·57
70 : 30	— 80	69·0	25·5	12·17
	— 180	78·5	32·8	13·2
Aluminium	R.T.	19·0	4·38	1·98
	— 80	20·0	5·30	1·90
	— 180	27·0	9·30	2·03

Soft solder was found to have lost practically all its resistance to impact at — 180° C., but its tensile strength and yield point were markedly increased.

CHAPTER VIII.

THE DESIGN AND CONSTRUCTION OF THE CHEMICAL AUTOCLAVE.

IN a chemical engineering sense, an autoclave may well be defined as a heated pressure vessel for carrying out chemical reactions involving the use of liquids, and in general the pressure obtained therein is due to the vapour pressure of the constituents when raised to the desired temperature.

The industrial chemical autoclave was first used in connection with the manufacture of synthetic dyestuffs, which were invented about the middle of the nineteenth century. Descriptions of early autoclaves were given in Chapter I.

Although English chemists can claim a very large share of the credit in connection with the early developments of the synthetic dyestuff industry, for reasons which are perhaps more of an economic than of a technical character, the commercial exploitation of many branches of this vital industry soon became a German monopoly, and in the years immediately prior to the Great War (1914) the whole world was to a large extent dependent upon that country for most dyestuffs and intermediates.

Hence, the technique of the design and operation of large high-pressure autoclaves used in the manufacture of these chemical products was to a large extent confined to steelmakers such as Krupp of Essen and the great German dyestuff corporations.

An interesting and somewhat disturbing commentary on the position of autoclaves in this country at the outbreak of war in 1914 was given by Mr. James Morton, the founder of Scottish Dyes Ltd., before the Royal Society of Arts in 1929, and which has since been published in book form under the title of "Fast Dyes and Dyeing." I commend it to all engaged in industrial chemistry as one of the most inspiring and encouraging addresses ever given before a learned society.

The following brief extract is of interest insofar as autoclaves are concerned, and I am greatly indebted to Mr. James Morton for permission to publish it.

In his endeavours to make his own vat colours for fast dyeing of textiles, and which, before the outbreak of war in 1914, he had purchased from Germany, he found that an autoclave to withstand pressures of 50-60 atms. was required to convert "silver salt" into 2-amino-anthraquinone, and this operation involved temperatures of 180-200° C. Mr. Morton states: "It involved one of the most difficult operations in chemical manufacture, and *one that had never been done in this country*—indeed, the means for it did not exist. By great luck we had available an old little autoclave made of Krupp steel, and which had been procured years before for quite a different purpose. It held about 1½ litres. . . . One cannot go into all the interesting and exciting details of these first days and nights, but suffice it to say that we at last got our little autoclave to yield quite respectable 2-amino-anthraquinone, and by November, just three months after war began, we had actually produced Indanthrene Yellow G, and a few days later Indanthrene Blue, only a few grammes of each, and I am afraid, not of the purest, but we had worked out the processes, and knew something of the road we had to travel, or shall I say, as much of it as was good for us then to know.

"We had to consider plant, and it made me smile, when looking up my notebook the other day in connection with this paper, to read the modest list of requirements that was to form the first chemical plant in this country for the making of vat dyes—a few hundred pounds sterling in all. The chief problem, as you may imagine, was the autoclave. We decided to make it of a size to hold a charge of 8 cwts., and a steel vessel of that capacity to stand a working pressure of 50 atms. at about 200° C. had never been thought of in this country. However, with the help of a good local engineer we made as careful a design as we could for an autoclave, complete with stirring gear, pressure gauge, thermometer pockets, safety valve, etc., and the casting was put into the hands of a London company, to whom we had been specially recommended. It was a long wait for this vessel, but meantime the other plant was getting ready, and we kept getting experience with our little autoclave, making a charge every day without fail, and the cupfuls of blue and yellow colour thus got were not to be despised. At last, some time in January, 1915, the wonderful autoclave was ready, and I went south to see the hydraulic test, but it was no good. The material used had been too porous; moreover, it had faults in construction, where the makers had departed from our design, and we decided that we could never take the risk of a charge with ammonia at the temperatures necessary. This was our first adverse blow.

"In an extremity we heard from an engineer of a certain vessel in London that might be adapted to this high pressure and temperature, and we lost several weeks in adapting this, to find it also insufficient.

"About this time I heard that one of the big dye firms had a vessel that might do such work, and I went at once to see if they could extend us temporary accommodation. I mention this incident because of its effect in other ways. The gentleman whom I saw seemed astonished at my visit and my request. What were we up to ? This was a chemical operation, and we were only weavers, or some such remarks rather in disparagement of people like ourselves trying to make dyes, especially dyes requiring such processes. From my after knowledge I learnt that he had really no plant that could have helped us, so that his methods may have been by way of a screen or bluff. But it had the effect of putting further fight into me, and 'Begad,' I said to my friend, who was waiting outside, 'I will let that man see whether weavers can make dyes.'

"But what about our autoclave ? The above incident was early in March. It was impossible to wait further months, for we were starving for colour, so we thought 'why not buy weldless steel tubing ? ' and we learnt that a length might be available at Cochran's Boiler Works at Annan. I can remember the very cold night on which we drove out to Annan on that quest, the keenness and determination of each of us, and we brought back in our car the tubing which is chronicled in my notes, under date just three weeks after the rebuff recorded above, as follows :—

"'*Saturday, March 27th*, 1915.—Have had satisfactory results, silver salt into 2-amino-anthraquinone from improvised autoclave made out of Stewart and Lloyd M.S. tubing 3′ 8″ long by 10″ diameter. Charge, 7 gallons silver salt and ammonia gave us sufficient amino for 20 lbs. of colour. Immediately put two other vessels in hand which should give us 60 lbs. per day, sufficient to dye 25-30 pieces of cloth of a medium blue or green.'

"It was one of the red letter days, and though the colour was by no means standard, it was the first real works blue and yellow vats produced in this country, made as you see at the works at Carlisle, and from plant practically all local. It was, as I have said, the real beginning ; for from that day we have never ceased getting our supplies from our own production. And it will give some idea of the growth from that small beginning when I tell you that of these two colours, or their variations, our plant has now a capacity of over 10 tons per week, or about a million lbs. per year.

"By October of that year, 1915, a thoroughly sound 8 cwt. autoclave with stirring gear and everything complete had come to the assistance of our little battery of tubing autoclaves. This was cast by Edgar Allen of Sheffield, and proved sound in every way. It was succeeded by one of a ton capacity, also made by the same firm, and later by some from Hadfield of Sheffield and others, most of which are still running.

"I have given you the history of these autoclaves in detail because they are one of the chief keys in the manufacture of vat dyes, and because they represented a problem in high-pressure and high-temperature reactions that were quite new to the chemical and engineering experience of this country, and that demanded a combined skill and knowledge of the highest order."

These early efforts of Mr. James Morton have been well rewarded, and eventually led to the foundation of Scottish Dyes Ltd., now a branch of Imperial Chemical Industries Ltd.

Happily, the position in Great Britain to-day is far more satisfactory than in 1914. With few exceptions, all dyestuffs used in this country are "made in Britain" and the design of suitable high-pressure plant does not now present the slightest difficulty. Such vessels can be obtained for the highest pressures from many British chemical plant manufacturers specialising in this type of equipment.

The first autoclave built by Edgar Allen & Co., Ltd., for Mr. Morton is shown in Fig. 167, and I am indebted to Messrs. Edgar Allen for permission to reproduce the actual working drawing, which is naturally of considerable historic, as well as technical, interest.

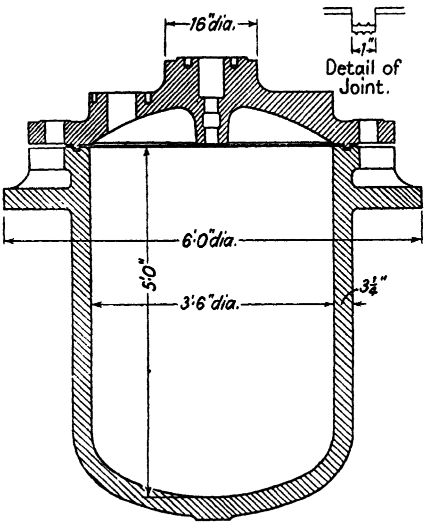

Fig. 167.—Edgar Allen autoclave (1915).

The autoclave body and end plate are of cast steel, and the designed working pressure was 700 lbs./sq. in. It is 3 ft. 6 ins. internal diameter, with walls 3¼ ins. thick, and is 5 ft. deep. The end plate is secured to the body by means of eighteen 3-in. diameter steel bolts and nuts, and the joint is of the spigot and recess pattern. The joint face is 1 in. wide, and an enlarged view of this is shown in the figure. The autoclave is fitted with a stirrer, and details of the dimensions of the stuffing box can be gathered from the drawing. Before being put into service, the autoclave was subjected to an hydraulic test pressure of 2000 lbs./sq. in.

The working temperature desired was not higher than 220° C., so that creep does not enter into the considerations affecting design stresses.

The cover plate is fitted with openings for the stirrer shaft in the

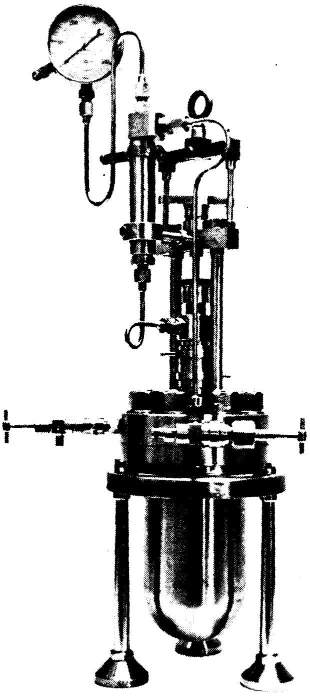

FIG. 168.—2-litre high-pressure autoclave. (Designed and built at the Chemical Research Laboratory.)

[*To face page* 279.

centre, a safety valve pressure gauge connection, manhole opening and thermometer pocket. All openings are closed by flanges (except, of course, the stirrer shaft opening), which are secured to the plate by studs and nuts.

There has been considerable activity in the design and construction of high-pressure autoclaves during the past fifteen years or so, and with the advent of new steels and alloys, which permit of higher working stresses, satisfactory designs have been evolved for considerable pressures and elevated temperatures.

Modern High-pressure Laboratory Autoclaves.

An example of a fairly large modern laboratory high-pressure autoclave is shown in the photograph (Fig. 168). It was designed and built at the Chemical Research Laboratory in 1929 for pressures of 250 atms. (3750 lbs./sq. in.) at temperatures not exceeding 425° C. The working capacity is a little over 2 litres, and the total weight, as assembled in the photograph, is 2½ cwts. About 0·3 h.p. is required to rotate the stirrer shaft at a speed of 150 r.p.m.

Insofar as the highly stressed parts are concerned, it was made from nickel-chrome-molybdenum steel of the following composition :

C	Mn	Si	S	P	Ni	Cr	Mo	Fe
0·3	0·57	0·24	0·03	0·028	2·53	0·62	0·65	Remainder per cent.

All the forgings for this autoclave were supplied by Thos. Firth & John Brown, Ltd., Sheffield.

The drawings (Figs. 169, 170 and 171) show the general design.

It will be seen that the body is 5-in. internal and 8-in. external diameter. This gives a ratio $\frac{D}{d}$ or $k = 1{\cdot}6$, whence $k^2 = 2{\cdot}56$. The working pressure is 250 atms. or 1·67 tons/sq. in., so that we can calculate the stress in the shell due to this internal pressure from

$$p = 0{\cdot}6f\frac{k^2 - 1}{k^2}.$$

Substituting $$1{\cdot}67 = 0{\cdot}6f\frac{2{\cdot}56 - 1}{2{\cdot}56},$$

whence $$f = 4{\cdot}6 \text{ tons/sq. in.}$$

Regarding temperature difference stresses, by considerable experience at Teddington it has been found that if the rate of heating up to the maximum temperature does not exceed 100° C. per hour, the difference in temperature between the outside and inside of such shells is not more than 20° C. For the material in question (nickel-chrome-molybdenum steel) at a temperature of 425° C., the expression

$\frac{mE\alpha}{m-1}$ is 440 (see Chap. VII., Fig. 166). This figure is not shown in the alignment chart, so we take $\frac{mE\alpha}{m-1}$ equal to 660, and take two-thirds of the stress so found. From the chart with $\frac{D}{d} = 1{\cdot}6$, and $\frac{mE\alpha}{m-1}$ equal to 660, we get a stress of 370 lbs./sq. in. per °C., giving a value of 247 lbs./sq. in. per °C. for our problem or a total stress of 247 × 20 = 4940 lbs./sq. in. or 2·2 tons/sq. in.

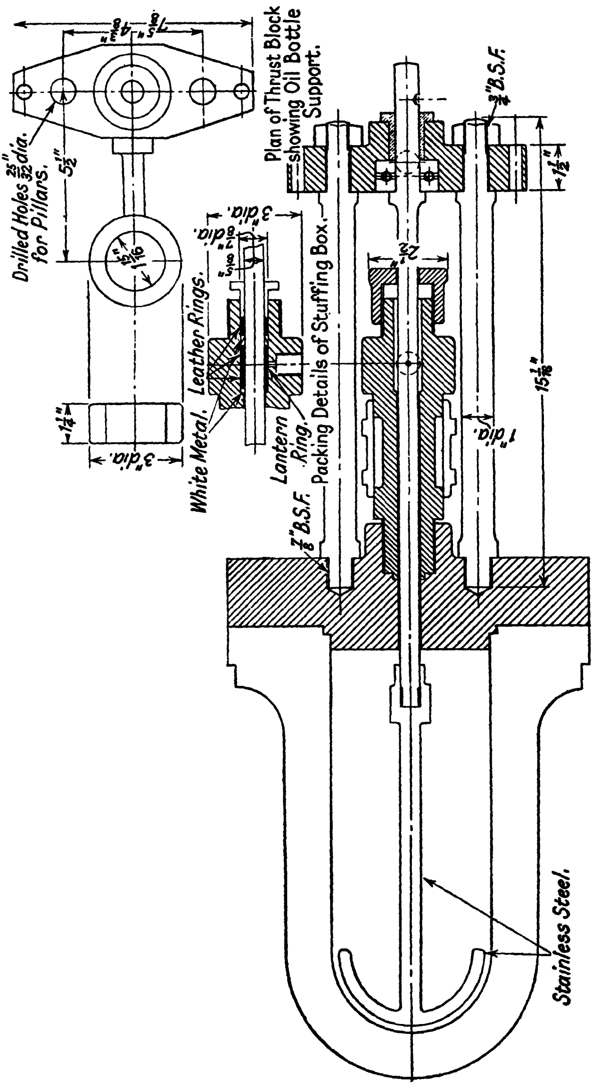

FIG. 169.—Section of C.R.L. 2-litre autoclave.

Thus the total hoop stress may be taken as 2·2 + 4·6 = 6·8 tons/sq. in.

Since the autoclave is externally heated by gas, at the maximum internal working temperature of 425° C., the outside temperature of the shell will be 445° C. or so, at which the "time-yield" value for this material (nickel-chrome - molybdenum steel) (see curve, Fig. 161) is 11 tons per sq. in. So that taking Dr. Hatfield's value of two-thirds of this, i.e. 7·3 tons as a safe working stress, we find that our designed working stress of 6·8 tons per sq. in. gives an ample factor of safety.

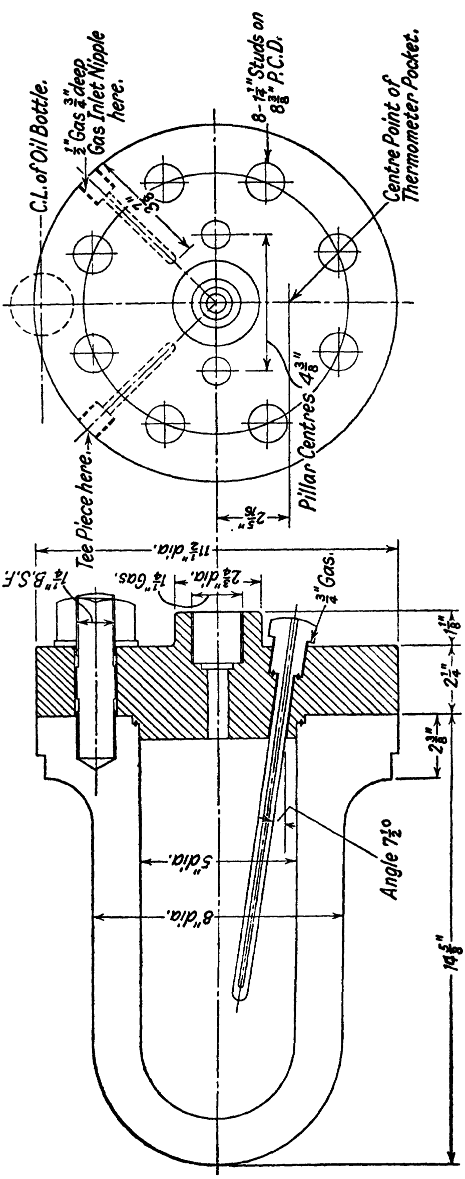

FIG. 170.—Details of body and end plate of C.R.L. 250 atm. 2-litre autoclave.

NOTE.—This autoclave was built some four years ago when long-time creep test data for this steel were not available. Recent research involving long-time tests has shown that stresses based on Hatfield's time-yield curves for this particular steel are quite satisfactory at the temperatures given. (For example see curve, Fig. 158.)

The end plate is secured to the body by eight 1¼ ins. B.S.F. studs and nuts; assuming that the internal pressure acts on an area enclosed by the outer circumference of the joint ring (i.e. one of 5½-in. diameter), the total upward pressure on this end plate due to the gas pressure is

$$\frac{\pi d^2}{4} \times p = \frac{22}{7} \times \frac{121}{16} \times 1{\cdot}67 = 40 \text{ tons.}$$

Since there are eight studs, this corresponds to a load of 5 tons per stud. Allowing 40 per cent. for tightening up stresses, it is concluded that this corresponds to a stress of 7·8 tons per sq. in.

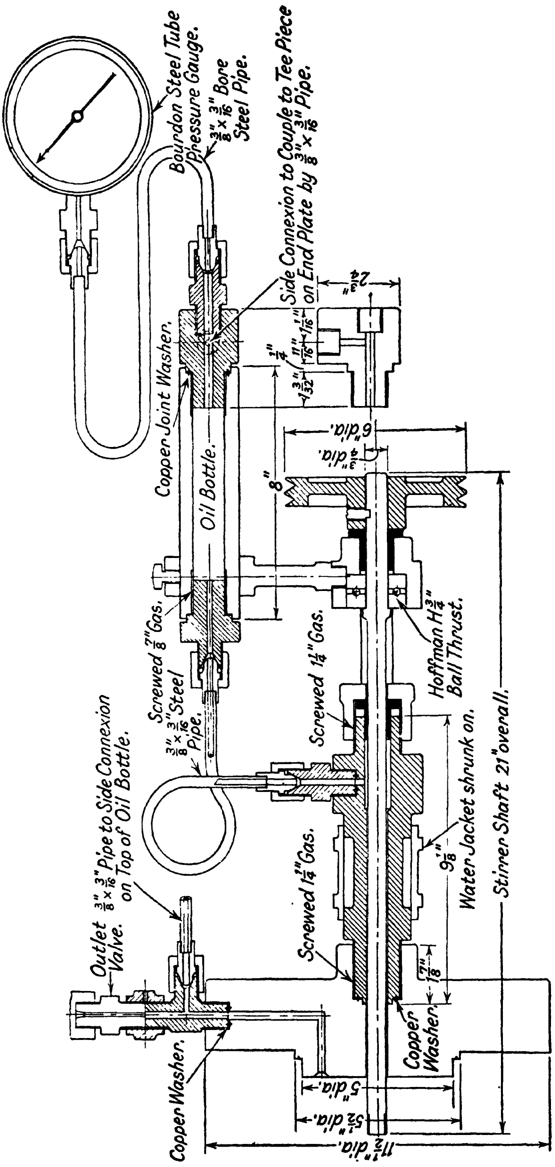

FIG. 171.—Details of end plate and stirrer shaft stuffing box, C.R.L. 250 atm. 2-litre autoclave.

The mean temperature of these studs is of the order of 400° C., when the interior is at 425° C., so that the permissible stress based on the "time-yield" is 9·3 tons per sq. in. Hence, there is a satisfactory margin.

With regard to the thickness of the end plate, if this were a plain plate it would be satisfactory if it were made the same thickness as the shell. Owing to the number of holes drilled in it, it was decided to make it $2\frac{1}{4}$ ins. thick to allow for the weakening effect of these holes. The joint between the end plate and the body is made on a copper washer, $\frac{1}{4}$ in. wide and $\frac{1}{32}$ in. thick, and which has been thoroughly softened by annealing before use. The copper washer is protected by two spigots from corrosive influences, and these spigots also serve to prevent " spreading " of the washer. Vee groves are turned in both joint faces $\frac{1}{32}$ in. deep × $\frac{1}{32}$ in. wide, and these materially assist tightness. After many years' experience with all types of joint for laboratory and small manufacturing scale autoclaves. I am of the opinion that this is by far the best.

The method of pulling down the end plate quite evenly by tightening on opposite sides of the cover was explained at length in Chapter IV.

The autoclave is fitted with a stirrer, which is in two parts. The lower part is the stirrer proper, and is made from stainless steel of the 18 : 8 type. This part is screwed to the stirrer shaft, and true alignment is secured by leaving a plain parallel portion in the hole of the anchor portion, as shown. The upper part of the stirrer, i.e. the shaft, is preferably made from one of the case-hardening steels, in order to present a smooth surface to the stuffing box packing rings. This stuffing box is yet another example of the use of the hydraulically sealed lantern ring. The stirrer shaft is $\frac{5}{8}$-in. diameter, and the bore of the stuffing box is $\frac{7}{8}$-in. diameter. (It is well not to make these boxes too wide. As narrow a ring of packing as is possible gives the best results.) The lantern ring and gland bush are of phosphor bronze. The packing is of leather and white metal, distributed as shown in the enlarged view. The leather washers are quite readily made from old leather belting, well soaked in tallow. The oil connection to the lantern ring is taken from the bottom of an oil bottle, which is maintained at the same pressure as that in the autoclave by a $\frac{3}{8}$-in. × $\frac{3}{16}$-in. steel pipe connected to both.

The pressure gauge is of the all-steel Bourdon type, with $\frac{1}{2}$-in. gas cone nipple connection, and it is fitted to the top of the oil bottle by means of a syphon pipe. The reason for this remote position is to screen the gauge from the heat of the autoclave, and also to minimise the amount of possibly corrosive gas entering the Bourdon tube by fitting an oil seal or syphon inside the pipe beneath it. The stuffing box is made from the same material as the body, end plate and studs, and is secured to the end plate by screwing home on a copper joint ring. The cover plate is fitted with a boss as previously explained, to counteract the weakening effect of the hole for the stuffing box. The gland nut is of mild steel, and is knurled and drilled for five ¼-in. tommy bar holes. A tommy bar 4 ins. long gives quite sufficient leverage to ensure packing tightness.

This type of stuffing box is fitted to all autoclaves built at the Chemical Research Laboratory, and it has never yet failed in actual practice. The oil is prevented from flowing or seeping down the stirrer shaft and so into the autoclave by the leather washers beneath the lantern ring. Viscous oil, with a low temperature-viscosity coefficient should be used, and oils of the heavy automobile type are quite satisfactory. The oil bottle is usually filled to 50-60 per cent. of capacity before an experiment, and this is sufficient to last during an experiment of two or three days' duration.

When running under pressure, there is a considerable thrust on the stirrer shaft tending to blow it out of the autoclave. This pressure or thrust is $\left(\frac{\pi d^2}{4} \times p\right)$ or $0{\cdot}7854 \times (\frac{5}{8} \times \frac{5}{8}) \times 1{\cdot}67$ tons $= 1150$ lbs. This considerable thrust is taken by a Hoffmann heavy ball thrust bearing (¾-in. diameter). This thrust bearing is housed in a mild steel block, which is supported from the autoclave cover plate by two 1-in. diameter steel pillars, screwed into the end plate. This thrust block also serves as the oil bottle support (see Fig. 171). A phosphor bronze bush is fitted to this thrust block to act as the upper bearing of the stirrer shaft, which here is ¾-in. diameter. The shaft is rotated by power belt drive to a pulley or to a coupling. The pulley is 6-in. diameter, and is grooved for a double ⅜-in. round belt drive, and 0·3 h.p. is more than adequate to drive this shaft at 150 r.p.m., even when dealing with viscous materials in the autoclave.

The end plate is also drilled with two ½-in. gas openings, one of which takes a tee-piece and the through-way of this leads to the gas release valve, for relieving excess pressure or for relieving the pressure upon the conclusion of an experiment. The sideway of the tee-piece serves as a pipe connection to convey the pressure inside the autoclave to the oil bottle, and is hence known as "a pressure balancing pipe." The other ½-in. gas opening in the cover plate is for a pipe connection, from a gas inlet valve, so that gaseous reagents may be introduced either before or during the course of an experiment. The cover is also fitted with a thermometer pocket, which is $\frac{3}{16}$-in. bore × ½-in. outside diameter. The pocket is drilled from a solid bar of nickel-chrome-molybdenum steel, and is screwed into the cover plate (at an angle) on a flat copper washer. This steel is a structural material, and has no special corrosion resisting properties, so to protect it from the influence of corrosion, it is fitted with a sheath of 18 : 8 stainless steel, which can be renewed quite cheaply.

To measure the temperature, an iron constantan thermocouple $\frac{5}{32}$-in. outside diameter is used.

To protect the walls of the autoclave from corrosive liquid reagents, a loosely fitting liner of 18 : 8 stainless steel, 16 gauge thick and $4\frac{15}{16}$-ins. outside diameter, is put inside the autoclave, and this also serves to facilitate removal of the contents after an experiment.

To prove quality and soundness of raw material, tests such as the following are specified for autoclave steels of the nickel-chrome-molybdenum type.

1. *Longitudinal tensile and impact tests of bar material,* i.e. studs and nuts, stuffing box, thermometer pocket, etc.

   Mechanical tests to give—

   Yield point, 45/50 tons./sq. in.
   Ultimate tensile, 55/60 tons./sq. in.
   Red. of area, 50 per cent.
   Elongation on 2 ins., not less than 20 per cent.
   Izod impact, not less than 50 ft.-lbs.

2. *Transverse tensile and impact tests of body and end plate forgings.* An extension is forged on the body forging and end plate forging, and transverse tensile and impact tests on these should give—

   Yield point, 45/50 tons./sq. in.
   Ultimate tensile, 55/60 tons./sq. in.
   Red. of area, 45 per cent. minimum.
   Elongation on 2 ins., not less than 15 per cent.
   Izod impact, not less than 28 ft.-lbs.

It is most important that all the highly stressed parts of an autoclave or similar vessel shall be made from the same type of raw material, in order that expansion due to heating shall be uniform. For example, it would be fatal to the case cited to use stainless steel forgings for body and end plate and nickel-chrome-molybdenum steel studs and nuts, because of the wide difference in their coefficients of expansion (see Table 20 in Chap. VII.).

It will be noted that this autoclave is not fitted with a safety valve. It is, of course, quite impossible to keep such fittings tight at pressures much above 30-40 atms., particularly when gases of even a slightly corrosive nature are being used. It would be impossible to do any quantitative work with such fittings; hence, they are omitted, and safety precautions of quite a different type are employed. The autoclaves are placed inside steel screens, and rope mattresses are used as an additional precaution. All controls are placed outside these screens and arrangements are such that there is no need to go behind these protective devices during an experiment. A safety valve would not prevent a sudden explosive rise of pressure, and in all other cases it is possible to relieve this pressure by opening the release valve.

Before being first put into service, autoclaves and accessories, including oil bottle, connecting pipes and all pressure fittings, should be subjected to an hydraulic test pressure, which is in excess of the working pressure. The 2-litre autoclave under consideration was tested to a pressure of 350 atms. Before, during, and after the test significant dimensions should be carefully measured, and any undue deflection should be investigated. The probable increase in diameter of the bodies of such vessels can be calculated from the stress applied. Records of such tests should be carefully kept.

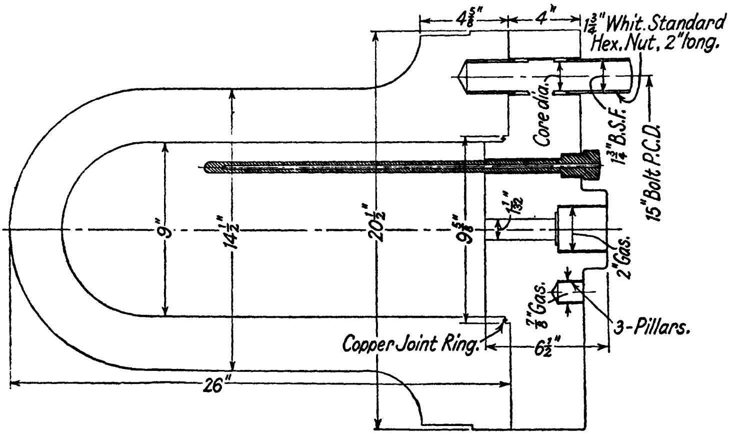

FIG. 172.—Detail of body and end plate of C.R.L. 250 atm. 12-litre autoclave.

It is advisable to test hydraulically such vessels at frequent intervals in order to note any deterioration. In cases when corrosive conditions exist, the body should be cleaned and examined periodically, and an allowance should be made in respect of original dimensions to allow for occasional light skimming of the bore to remove corrosion.

The procedure recommended for such hydraulic tests was described in Chapter IV., which also contains a full description of a suitable hydraulic test pump.

The 2-litre autoclave just described may be taken as typical of the high-pressure autoclaves designed and built at the Chemical Research Laboratory. Other sizes have been made with working capacities of 25 c.c. to 12 litres.

The body and end plate of the large 12-litre autoclave are shown in the drawing (Fig. 172), and a photograph of the complete auto-

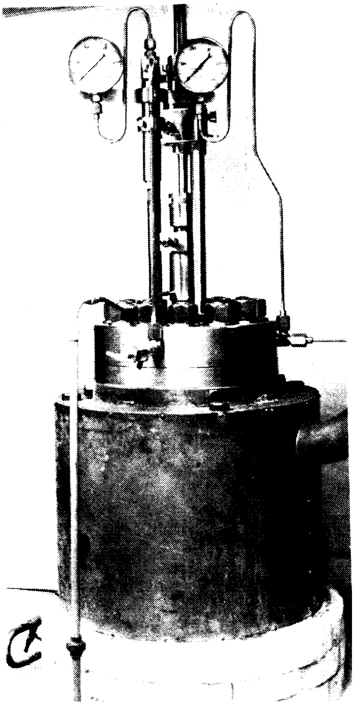

FIG. 173.—C.R.L. 12 litre autoclave.

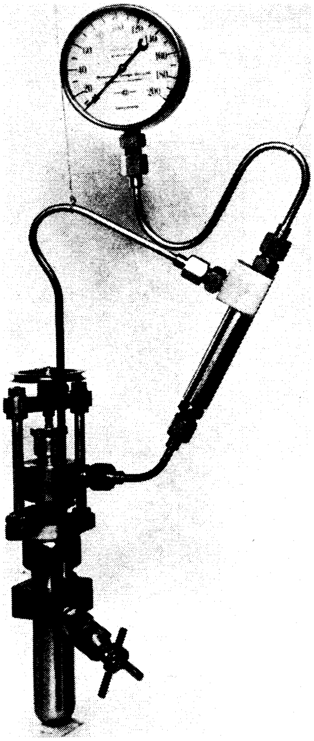

FIG. 174.—C.R.L. 25 c.c. autoclave.

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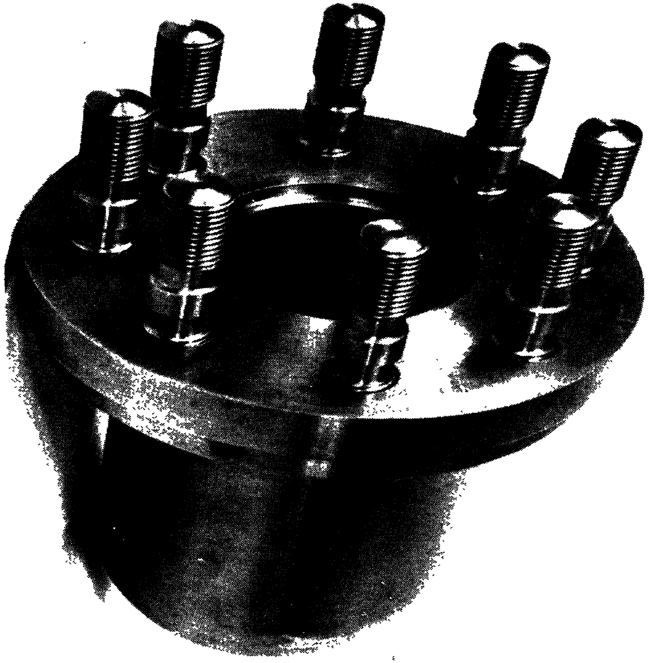

FIG. 176.—Body of C.R.L. 600 c.c. autoclave.

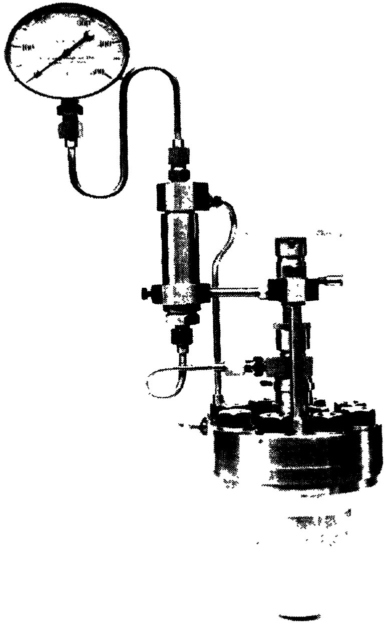

FIG. 175.—C.R.L. 600 c.c. autoclave.

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clave is shown in Fig. 173. It is suitable for working pressures of 250 atms. at temperatures not higher than 425° C. It is designed on lines very similar to the 2-litre autoclave, but, of course, all dimensions are appropriately increased. For example, the stuffing box is made to accommodate a 1-in. diameter stirrer shaft, and three pillars, instead of two, are fitted to carry the thrust block, the bearing of which is 1¾ in. diameter. It will be noted that the internal diameter of the autoclave is 9 ins., and the outside diameter 14½ ins., giving a ratio of $\frac{D}{d}$ or $K = 1{\cdot}61$, which is practically the same as in the case of the 2-litre autoclave. Therefore, all the calculations in connection with pressure and "temperature difference" stresses will give the same numerical result insofar as the shell hoop stress is concerned, i.e. 6·8 tons/sq. in. In order to keep the difference of temperature between the outside and inside to 20° C., or less, the rate of heating will, of course, have to be correspondingly reduced, owing to the extra thickness of metal, which is nickel-chrome-molybdenum steel.

It is interesting to calculate the considerable upward pressure on the end plate under working conditions, in the case of this autoclave. Taking the outside diameter of the joint ring as 9⅝ ins., and the pressure of 1·67 tons/sq. in. as the working pressure, the upward pressure on the cover plate is 120 tons.

The cover plate is secured to the body by means of twelve 1¾-in. B.S.F. studs and nuts, and the stress in these is 6·75 tons/sq. in. (allowing 30 per cent. additional stress for tightening up). The stirrer shaft in this case revolves at 80 r.p.m. In working order, without heating bath, this autoclave weighs 1525 lbs.

At the other end of the scale is the very small autoclave shown in Fig. 174, and which has a working capacity of 25 c.c., and a working pressure of 120 atms., at maximum temperature of 200° C. It was made from material very similar to that described for the 2-litre autoclave. The closure of the autoclave is effected by a plug, which is pulled home against a copper washer with a substantial hexagon cap nut. The stirrer shaft is ⅜-in. diameter, and is fitted with a lantern ring type of stuffing box, suitably proportioned for the small shaft. This autoclave is heated by an oil bath, and as there is no room to fit a thermocouple tube the temperature of the oil is taken as a basis for estimating the interior temperature.

As an example of the intermediate sizes, Figs. 175, 176, 177 show an autoclave for a working capacity of 600-750 c.c., and working pressures of 250 atms. and 450° C., as maximum temperature. Fig. 176 shows the body, and Fig. 177 the end plate, in which the method of jointing is very clearly brought out. This is made from a very interesting steel containing 0·5/1·0 per cent. molybdenum, and the composition usually includes small percentages of chromium and copper.

The material possesses good high temperature characteristics, and it is not affected by brittleness after prolonged heating at the temperature desired in the case under consideration (450° C.)

Its mechanical properties at room temperature in the normalised condition are :—

Yield Point. Tons/sq. in.	Max. Stress. Tons/sq. in.	Elong. on 2 in. per cent.	Red of Area. Per cent.
23·8	33·2	34·5	65·8

Izod Impact. Ft.-lbs.	Brinell Hardness.
87	145

This steel is made by Hadfields and is known as ERA 131. (See Table 8, Chap. VII., for creep data.)

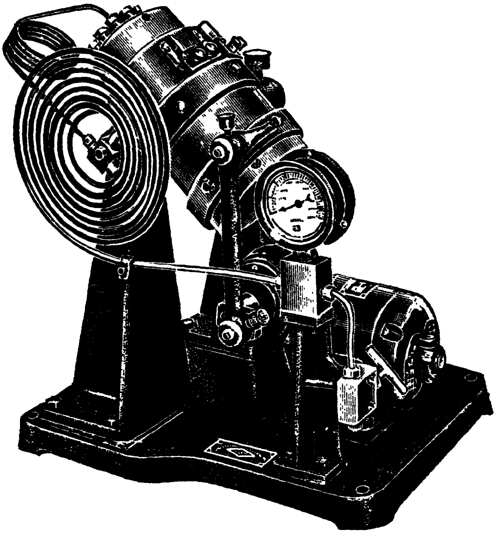

Fig. 179.—1000 atm. shaking autoclave. (American Instrument Co. Ltd.)

This 600 c.c. autoclave is very similar to the 2-litre autoclave. The inside diameter of the body is 3¼ ins., and the outside 5⅜ ins. The stirrer shaft is ½-in. diameter, and the speed of stirring is 180 r.p.m. The cover is secured by eight ⅞-in. Whitworth studs and nuts. A photograph of a section of the gland of one of these 600 c.c. autoclaves is given in Fig. 178.

All these autoclaves (with the exception of the 25 c.c. autoclave) are heated directly by gas. They are required for such a wide variety of work that gas is the only suitable method. The autoclave body is fitted inside a lapwelded steel tube, which is heavily lagged. The

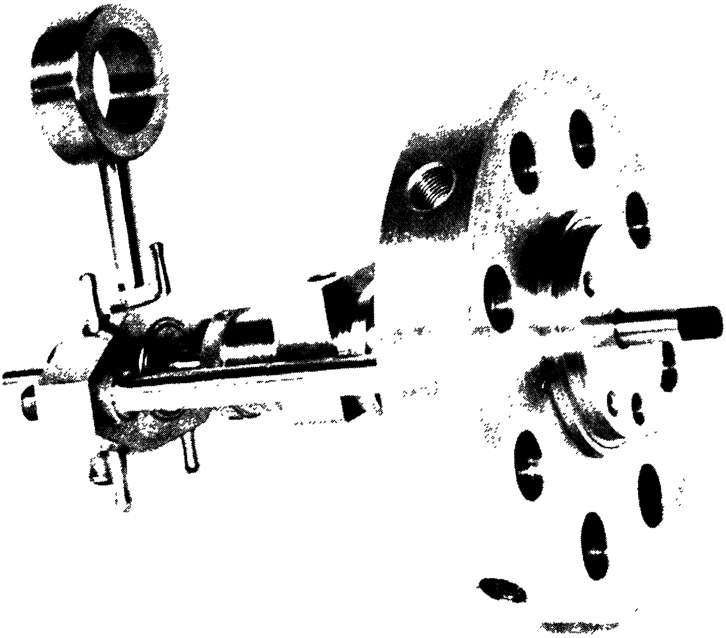

FIG. 177.—End plate of C.R.L. 600 c.c. autoclave.

[*See page* 287.

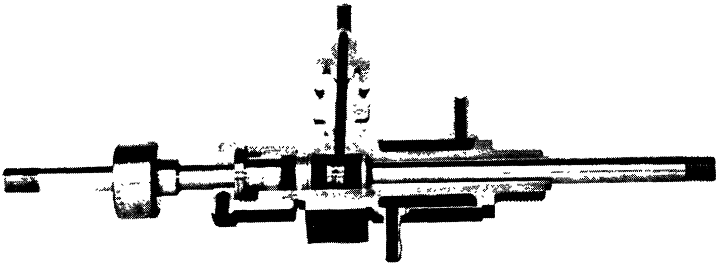

FIG. 178.—Photo of section of stuffing-box for stirrer shaft C.R.L. 600 c.c. autoclave.

[*To face page* 288.

gas burner, of the ordinary radial type, is fitted beneath the autoclave, but to prevent local overheating of the lower part of the autoclave, this is protected by a baffle.

The autoclaves of the type just described at the Chemical Research Laboratory include five of the 600 c.c. size and four of the 2-litre size.

A shaking autoclave made by the American Instrument Co. for pressures of 1000 atms. and a temperature not exceeding 752° F. is shown in Figs. 179 and 180. This type of autoclave is suitable for hydrogenation work. It is rocked through an angle of 30° at rates varying from 24 to 72 times per minute. The autoclave is held in place by a single bolt through the bottom of the outer retaining cylinder, and can be removed for recharging simply by loosening the bolt and breaking the pressure connection. The electrical heating element surrounding the autoclave is also quite quickly removed.

The assembled mechanism occupies a space of about 20 × 22 ins., and weighs about 250 lbs. Rocking of the autoclave is carried out by a ¼ h.p. electric motor. Heaters are usually wound for four heats.

The autoclave is machined from a piece of chrome-vanadium steel. The pressure connection may be brought in either through the body or through the head of the bomb. The head is composed of an outer cap that screws on the outside of the body of the bomb, and carries the thrust bolts, an inner pressure head bearing a copper washer for sealing and a hardened steel thrust ring to keep the thrust bolts from moving the pressure head. The cap is pierced by two holes for a spanner wrench for loosening, and with two tapped holes for eyebolts, for use in lifting the autoclave from the heating jacket. The pressure head carries a thermometer or thermometer well, as shown.

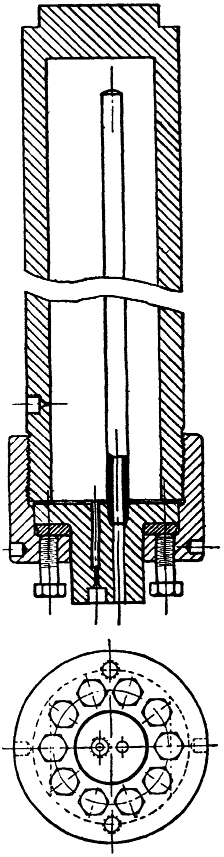

FIG. 180.—Detail of body of 1000 atm. shaking autoclave. (American Instrument Co. Ltd.)

Fig. 181 shows a rotating autoclave built by Andreas Hofer. It is gas heated and is fitted with a pulley for round belt or chain drive. The speed of rotation is about 10-15 r.p.m., and the stirring action may be assisted by the use of balls of steel or other suitable material.

This type is made in sizes from 1½ to 20 litres, and for pressures of 300 atms., at 550° C. The power required for rotation varies from ¼ h.p. in the smallest sizes to ½ h.p. for the 20-litre type.

The joint between the end plate and the body is made on the Ipatieff principle, i.e. a disc held between two knife edges, and the cover is secured by bolts. A thermometer pocket, pressure gauge and gas valve are fitted as standard.

A vertical autoclave with stirrer also made by Hofer is shown in Fig. 182. In Siemens-Martin steel these autoclaves are made in a range of sizes from 0·5 to 100 litres, and for working pressures of 300 atms. They are also made in Krupp V2A or V4A (corrosion-resisting austenitic steels), with capacities from 0·5 to 5 litres, again for maximum working pressures of 300 atms.

The joint between the cover and the body is made on the spigot and recess pattern, and bolts are employed to secure the cover to the body. The autoclave is gas heated and a reflux condenser with outlet valve is fitted. Temperature of the interior is taken by thermometer or thermocouple inserted in the thermometer tube. As in the case of the autoclaves previously described as installed at the Chemical Research Laboratory, the autoclave stirrer shaft is fitted with a lantern ring stuffing box fed by oil from an oil bottle maintained at the same pressure as that obtained in the autoclaves. The pressure pipe work for this purpose is clearly seen in the figure. The stirrer shaft pulley is driven by round belt.

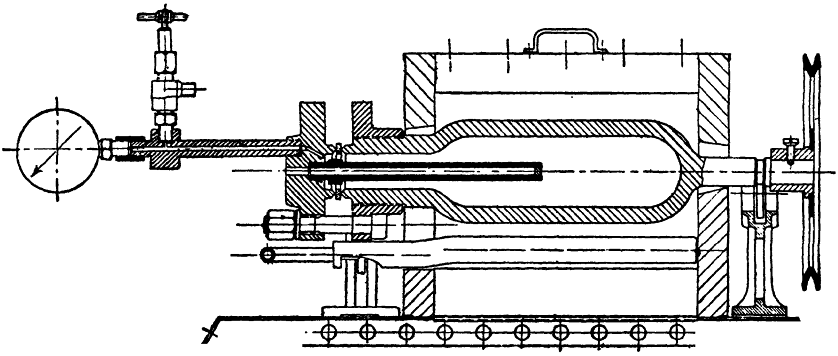

FIG. 181.—Hofer rotating gas heated autoclave.

Another similar type of autoclave, as made by Hofer, is shown in Fig. 183. It is very similar to that just described except that electric heating is used, the joint of the cover to the body is made on a double cone, and the stirrer shaft is driven by bevel gears.

In the larger sizes (50-100 litres) these autoclaves are fitted with flanged stuffing box bolted to the cover plates. This can be removed and the interior of the autoclave cleaned without disturbing the heavy main cover.

Hofer has developed a series of special stuffing boxes, or appliances for use with (*a*) impure or dirty liquids which attack the shaft, (*b*) oil sensitive liquids where oil falling down the stirrer shaft would spoil the product, and (*c*) substances which dissolve oil, etc., and render the ordinary lantern type difficult to keep tight.

Details of a Hofer vertical autoclave fitted with this special form of gland are shown in Fig. 184 and the following is a description of the method of operation :—

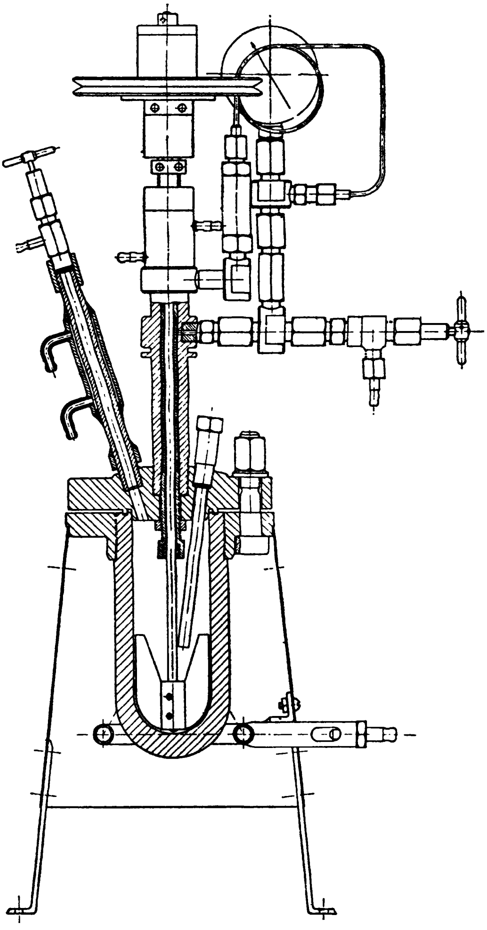

FIG. 182.—Hofer vertical gas heated autoclave.

Before putting the autoclave to work, the oil chamber " a " should be filled with oil to about 5 mm. below the level of the bottom of the filling plug " b ". (For large glands the oil capacity is increased by fitting a chamber " a_1" either vertically or horizontally.) The oil recommended is of the heavy cylinder type, or castor oil.

Before heating is commenced, it should be noted that water is flowing freely through the jacket " c."

If, during normal working conditions, an excessive amount of oil should leak past the gland nut " d," this may be tightened accordingly. Leakage of gas round the threads of this gland nut means that the oil supply in the oil chamber is exhausted, and this must be refilled in such circumstances. (Naturally, it is necessary to release the gas pressure in the autoclave before refilling.)

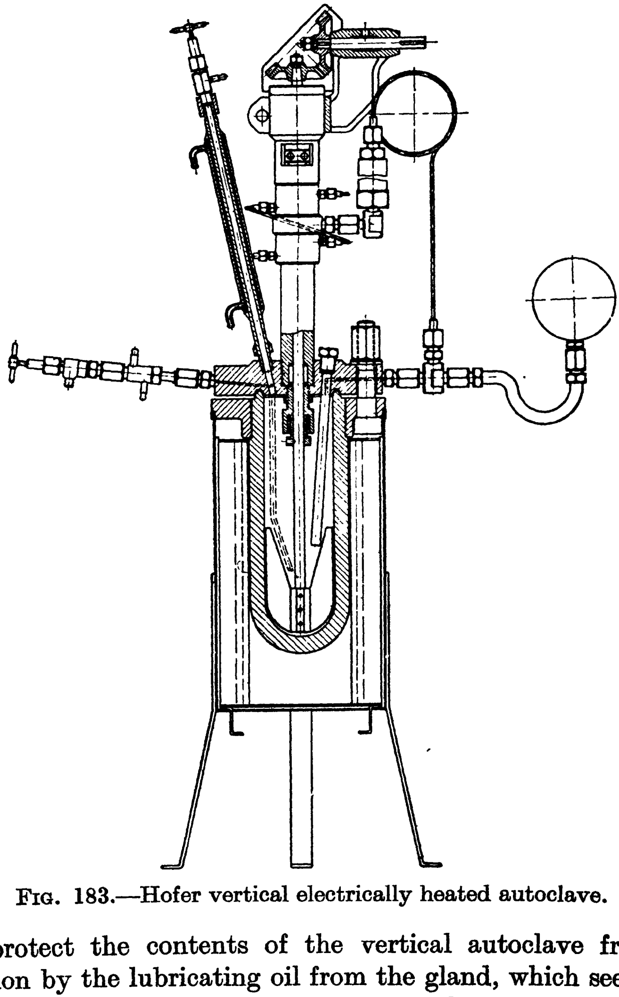

FIG. 183.—Hofer vertical electrically heated autoclave.

To protect the contents of the vertical autoclave from contamination by the lubricating oil from the gland, which seeps down the shaft, an oil collecting and separating chamber " e " is fitted. An opening " f " from the side of the autoclave cover leads into this chamber " e," and the other end of the drilled hole " f " is closed by a valve, which may be opened from time to time to test whether an excessive amount of oil is seeping down the shaft.

For work with oil-dissolving substances, i.e. where the vapours of such substances would destroy the lubricating properties of the oil for the gland, Hofer fits a special preliminary or fore gland "g." Fresh gas entering the autoclave (e.g. hydrogen in the case of hydrogenation experiments) is led through the chamber " h " through which such oil-dissolving vapours are led back to the body of the autoclave. In this way the parts of the stirrer mechanism are not exposed to the deteriorating action of oil-dissolving vapours or corrosive gases.

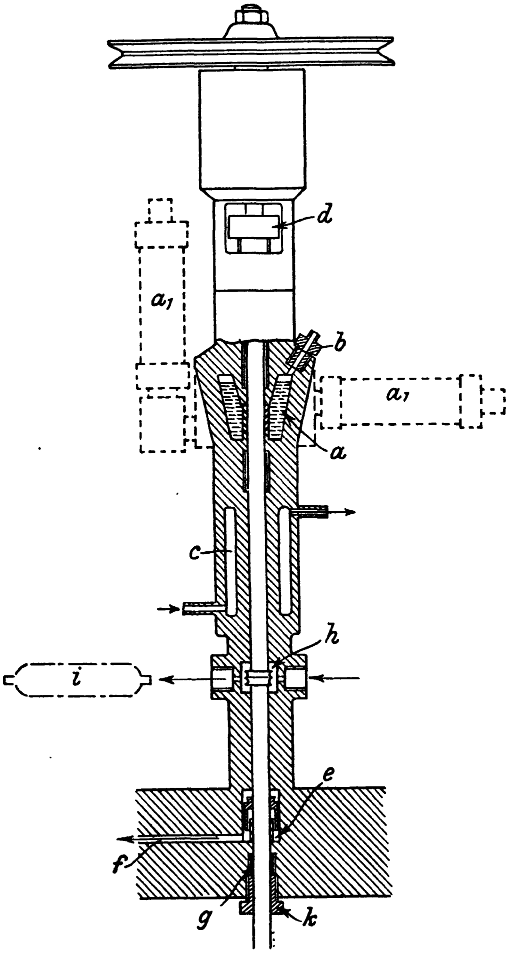

FIG. 184.—Special autoclave stirrer shaft stuffing box. (Andreas Hofer.)

Liquid settling in the chamber " h " (from both the gland oil and the condensed autoclave vapours) is collected in a separating bottle " i " fitted to this chamber. Excessive amounts of liquid deposited in the receiver means that the glands must receive attention.

In the case of horizontal autoclaves in which solids in the form of powders often form part of the reaction mixture, this preliminary or fore gland protects the working parts of the stirrer shaft from the abrasive action of such powders.

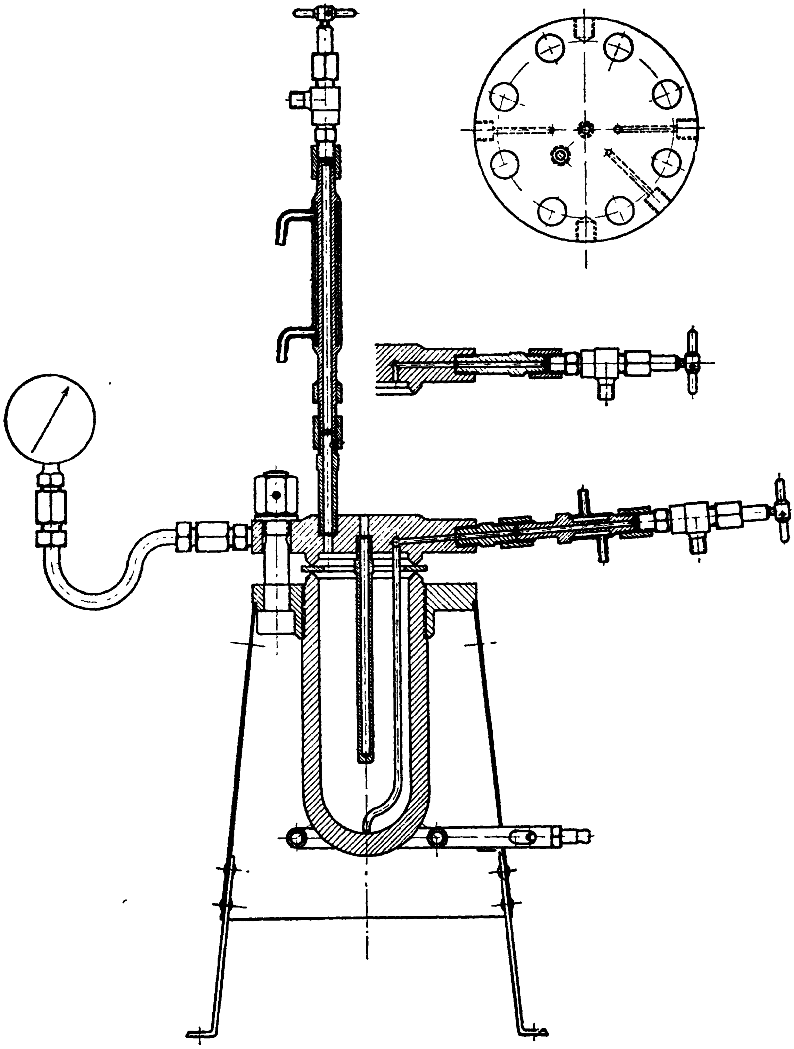

FIG. 185.—Hofer vertical autoclave with Ipatieff joint.

NOTE.—In the designs of autoclaves developed by the Chemical Research Laboratory oil is prevented from entering the autoclave by a sufficient number of leather rings beneath the lantern of the stuffing box.

An illustration of a Hofer vertical autoclave without stirring gear, and with a cover joint on the Ipatieff principle, is seen in Fig. 185.

It is gas heated and the general arrangement of the apparatus is clear from the drawing.

A horizontal high-pressure autoclave by Hofer with stirring gear is shown in Fig. 186. These can be supplied in capacities up to 5 litres and for working pressures of 300 atms. or so, as standard, but considerably larger sizes are available if required. They can be supplied in mild steel, structural alloy steels, or 18 : 8 stainless type of steel. The stirrer can be fitted if required with the special type of gland just described.

High-speed Stirring of Autoclaves.

In the case of many autoclave reactions, the rate of reaction depends upon the speed of the stirring device. Calvert (U.S. Patent 1,123,092 of 1914) describes an apparatus in which the stirring motor is inside the autoclave, and hence very high speeds are possible.

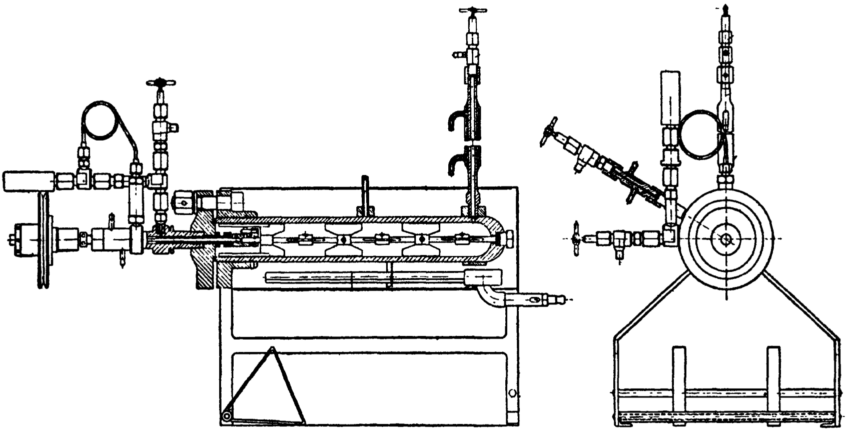

FIG. 186.—Hofer horizontal autoclave with stirring gear.

Recently McMillan and Krase have described a development of Calvert's suggestion, especially suitable for research purposes at higher pressures than were contemplated by Calvert (*Ind. Eng. Chem.*, 1932, **24**, 1001).

The top section (see Fig. 187) shows a vertical section through the apparatus which consists of three separate cylindrical sections. The top section is 9-in. outside diameter and $4\frac{7}{16}$-in. inside diameter, is 10 ins. long and the end plate is secured to the body by means of eight $\frac{3}{4}$-in. studs. This upper section contains the field and armature of a $\frac{1}{20}$ h.p. 110 v. 1750 r.p.m. motor, the shaft of which is $\frac{3}{4}$-in. diameter at the upper end, tapering down to $\frac{1}{4}$ in. at the lower end, and is 27 ins. long.

Three electrical leads pass out through the head, and are sealed by Bakelite compression cones in the usual way.

The middle section of the apparatus is 3-in. outside diameter, $\frac{7}{8}$-in. bore and 10 ins. long. The function of this section is to act as a reflux condenser for vapours evolved by the reaction, and hence to protect the motor parts. Water cooling passages are shown in the figure.

The lower section of the reaction chamber has the following dimensions: length 10 ins., outside diameter 3 ins., inside diameter $1\frac{5}{8}$ ins. The lower flange is held to the body by six $\frac{1}{4}$-in. cap screws.

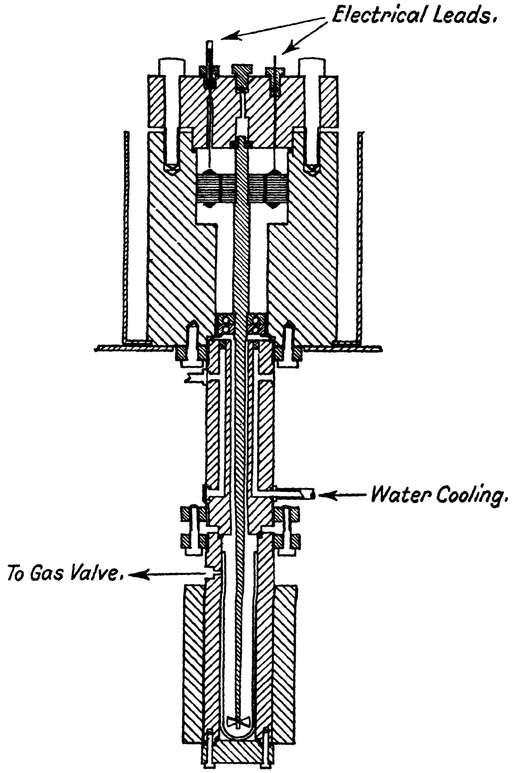

FIG. 187.—Autoclave with high-speed stirring gear.

Holloway and Krase subsequently described an interesting series of experiments on the synthesis of benzaldehyde in an apparatus of this character. Pressures of 1000 lbs./sq. in. were employed, and the temperature of the reaction chamber was of the order of 25-50° C. The reagents employed were benzene and carbon monoxide in the presence of aluminium chloride (*Ind. Eng. Chem.*, 1933, **25**, 497).

Large Autoclaves.

As an example of the stressing of autoclaves on a commercial scale, Fig. 188 shows an autoclave made as a hollow forging by Thos.

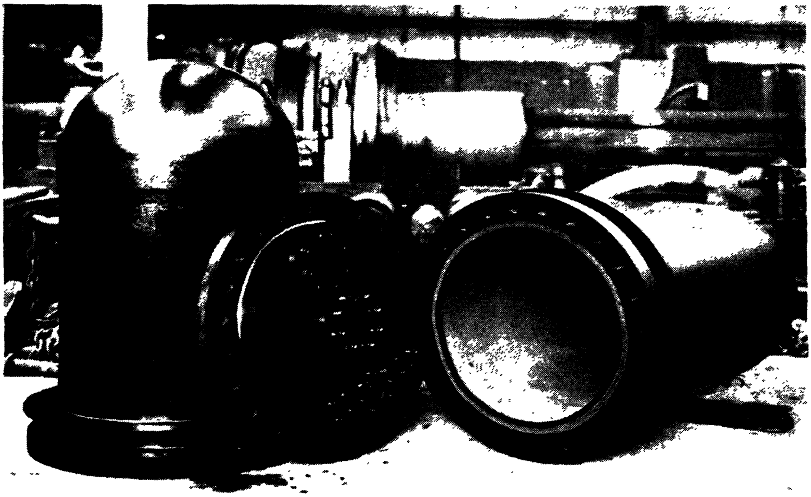

FIG. 188.—Forged steel autoclave. (Thos. Firth & John Brown, Ltd.)

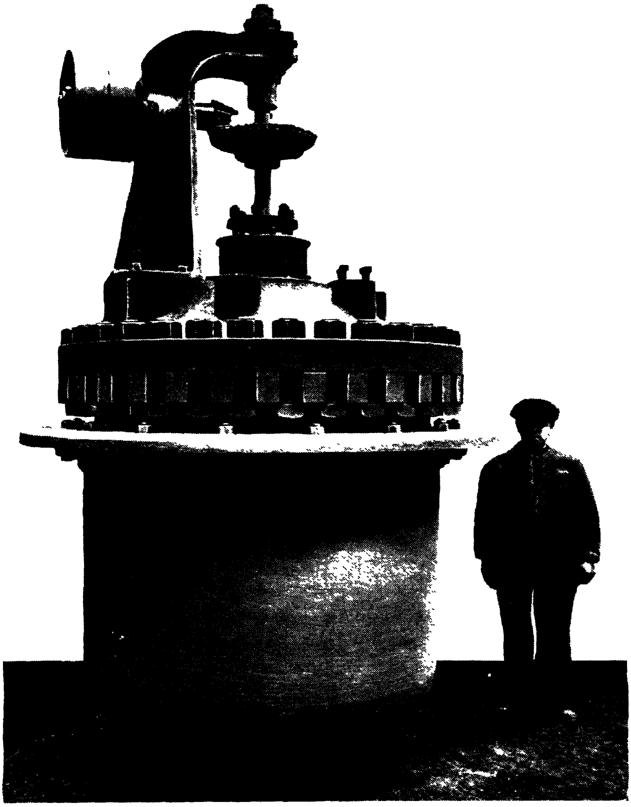

FIG. 189.—Autoclave of special toughened cast steel. (Hadfields Ltd.)

[*See page* 297.

[*To face page* 296.

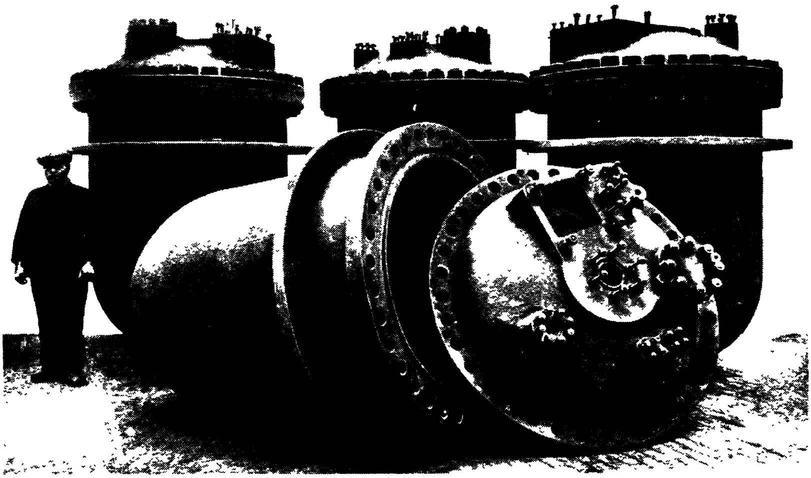

FIG. 190.—Group of autoclaves. (Hadfields Ltd.)

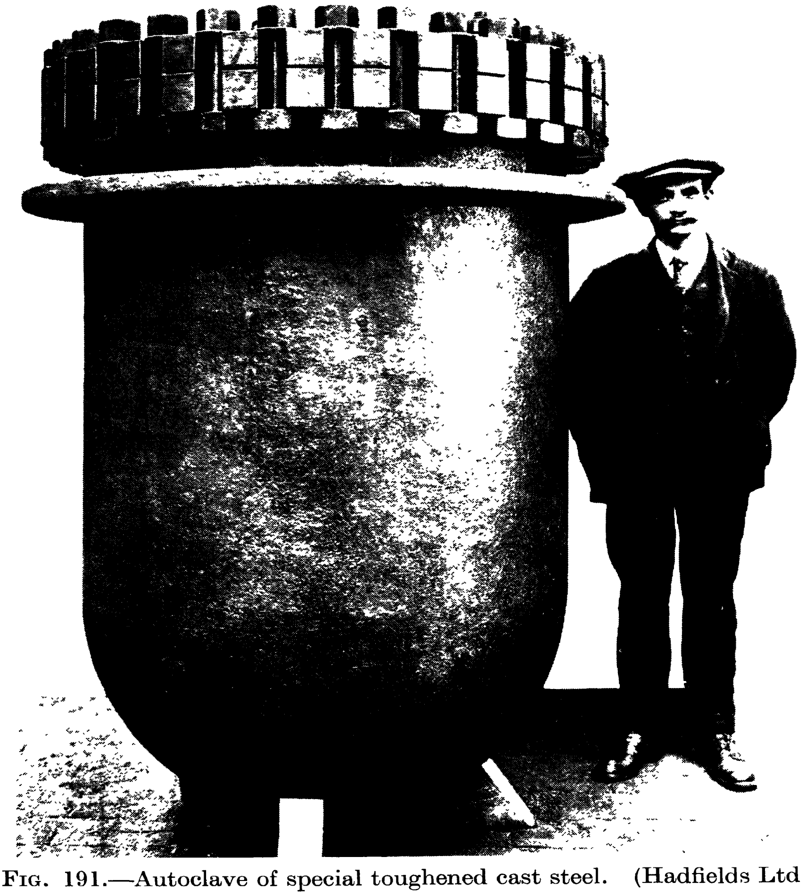

FIG. 191.—Autoclave of special toughened cast steel. (Hadfields Ltd.)

[*To face page* **297.**

Firth & John Brown, Ltd. It is 31¼-in. internal diameter, 5 ft. 5¾ ins. long, and with a wall thickness of 2 ins. It is in carbon steel, and designed for pressures of 1000 lbs./sq. in. at temperatures at which creep is unimportant.

Other examples of large autoclaves are shown in Figs. 189, 190, 191, 192. These autoclaves are of Hadfield's toughened cast steel. The dimensions are :—

	Working Pressure. Lbs./sq. in.	Inside Dia.	Wall Thickness.	Capacity. Gallons.
(1) Fig. 189 .	700	3′ 6″	3½″	280
(2) Fig. 190 .	500	4′ 0¼″	2½″	448
(3) Fig. 191 .	450	3′ 0″	2″	198
(4) Fig. 192 .	400	2′ 7¼″	2½″	163

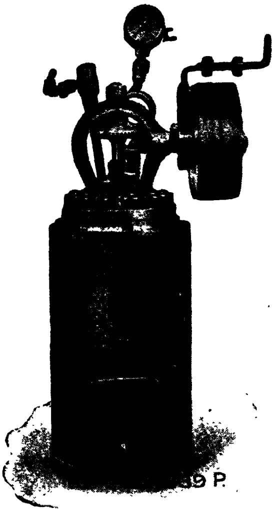
FIG. 193.

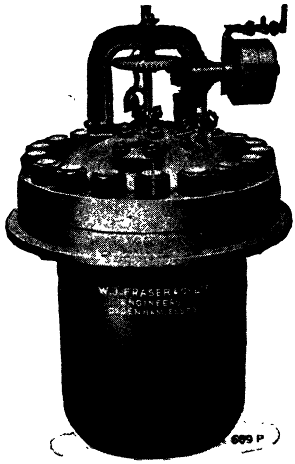
FIG. 194.

Again, these vessels are not subjected to temperatures within the "creep" region.

It will be noted that in all these cases the joint between the end plate and the body is made on the spigot and recess principle.

Fig. 193 shows a vertical cast steel autoclave made by W. J. Fraser & Co., Ltd., of Dagenham, Essex. It is heated by means of an oil bath, and is suitable for a working pressure of 3000 lbs./sq. in. A similar (but a little larger) autoclave made by the same firm for pressures of 1500 lbs./sq. in. is shown in Fig. 194. It is suitable for pharmaceutical and dyestuff work. It can be supplied for oil bath, steam jacket, or direct fired methods of heating as desired.

A vertical forged steel autoclave for fine chemical production at pressures up to 1000 lbs./sq. in., and also made by Fraser & Co., is illustrated in Fig. 195. It is steam jacketed, and provided with an easily opened cover (note swing bolts securing cover to body of autoclave), as the process is of very short duration and the material must be quickly removed after treatment.

Messrs. Fraser also manufacture horizontal high-pressure autoclaves, as shown in Fig. 196. The type shown was designed for the manufacture of synthetic drugs. It is steam jacketed and fitted with a powerful worm-driven stirrer. The working pressure is 1500 lbs./sq. in.

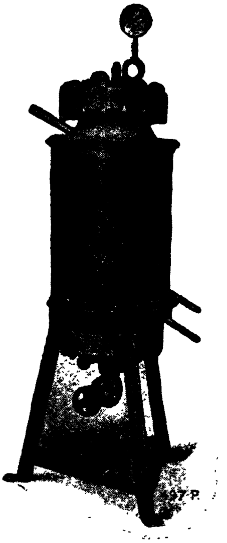

FIG. 195.

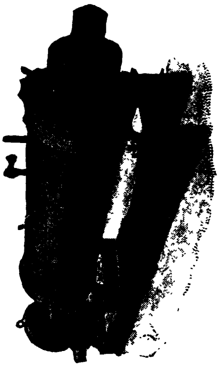

FIG. 196.

AUTOCLAVES FOR VERY HIGH PRESSURE.

Few autoclaves have been built for pressures exceeding 500 atms. or so, and the use of such very high-pressure autoclaves is confined to experimental work.

An autoclave for 3000 atms. pressure which has been designed and built at the Chemical Research Laboratory is shown in Figs. 197 and 28 (Chap. II.). It is $\frac{3}{4}$-in. bore, 11-in. outside diameter and $20\frac{1}{2}$ ins. long, and weighs with end plate, etc., attached, over a quarter of a ton. It is, so far as I know, the biggest autoclave ever built for such pressures. The internal capacity is 110 c.c. By

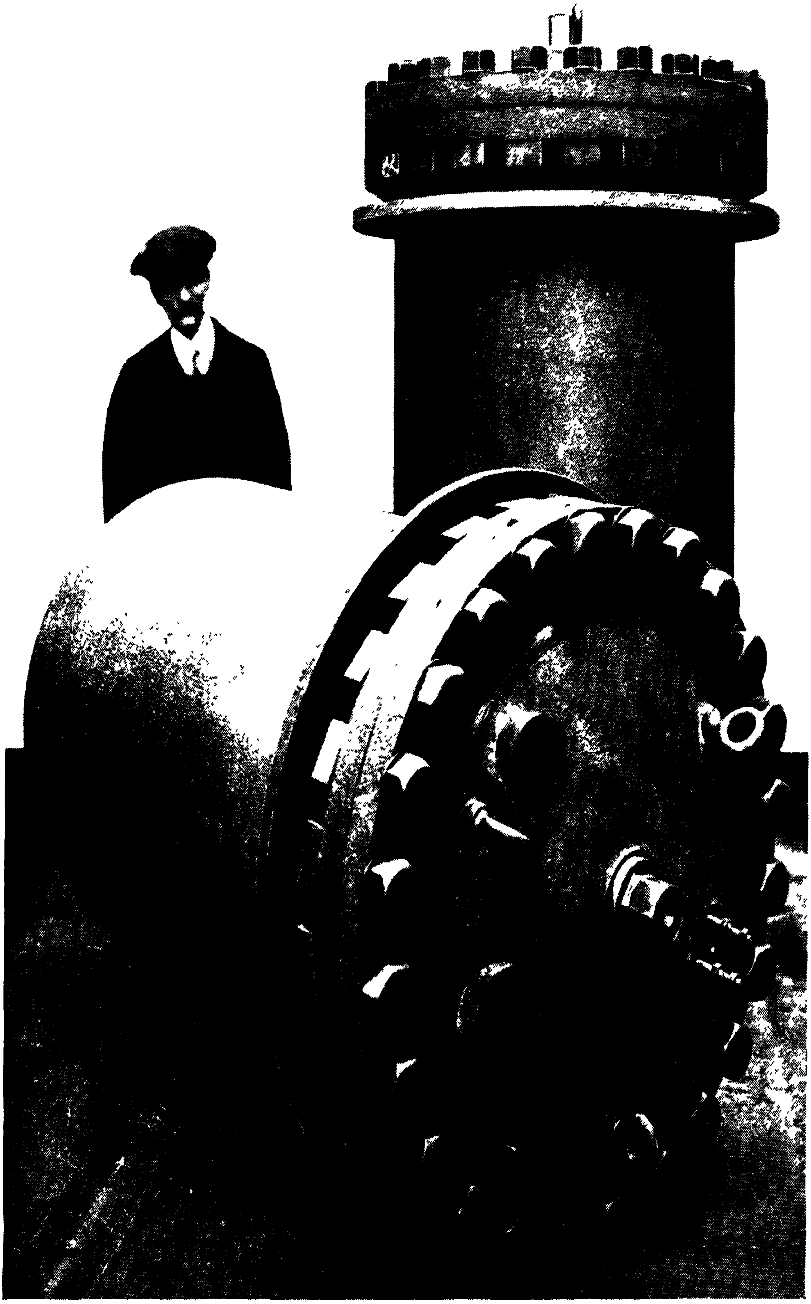

FIG. 192.—Autoclaves of special toughened cast steel. (Hadfields Ltd.)

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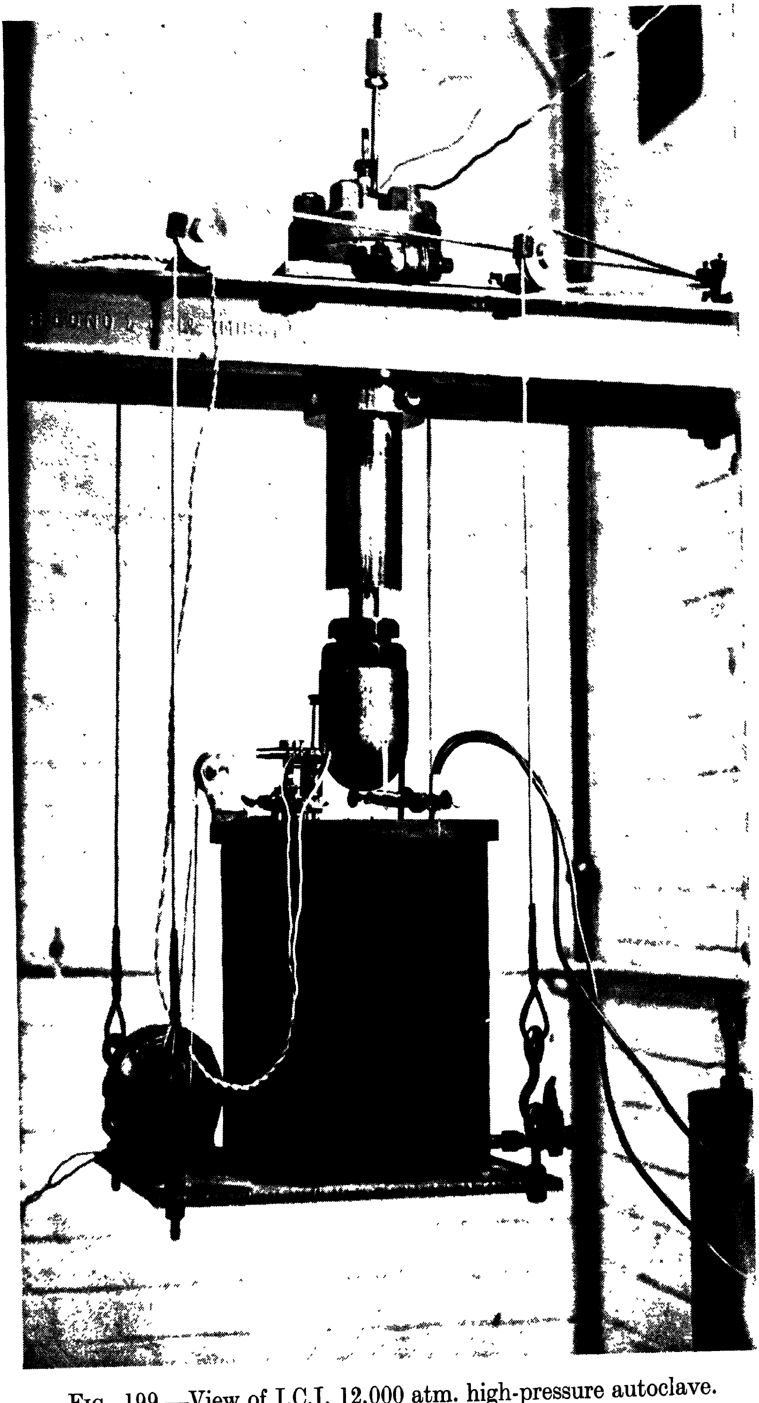

FIG. 199.—View of I.C.I. 12,000 atm. high-pressure autoclave.

[*See page* 301.

autofrettage it would be possible to use this autoclave up to 15,000 atms., but the pressure region of 3000 atms. is being explored before the higher ranges are considered.

The top end of the autoclave is sealed by an end plate, which is secured to the autoclave body by eight-1¼-in. studs and nuts. The joint is of the spigot and recess pattern, exactly as developed at the C.R.L. for the lower pressure autoclaves. The joint face diameter is 1¼ ins. and the jointing material used is soft annealed copper. The maximum working temperature of the autoclave, which is heated by an oil bath, is 150° C. The lower end of the autoclave is sealed by a valve, with a loose seating, and the joint is precisely the same as that described for the top end plate.

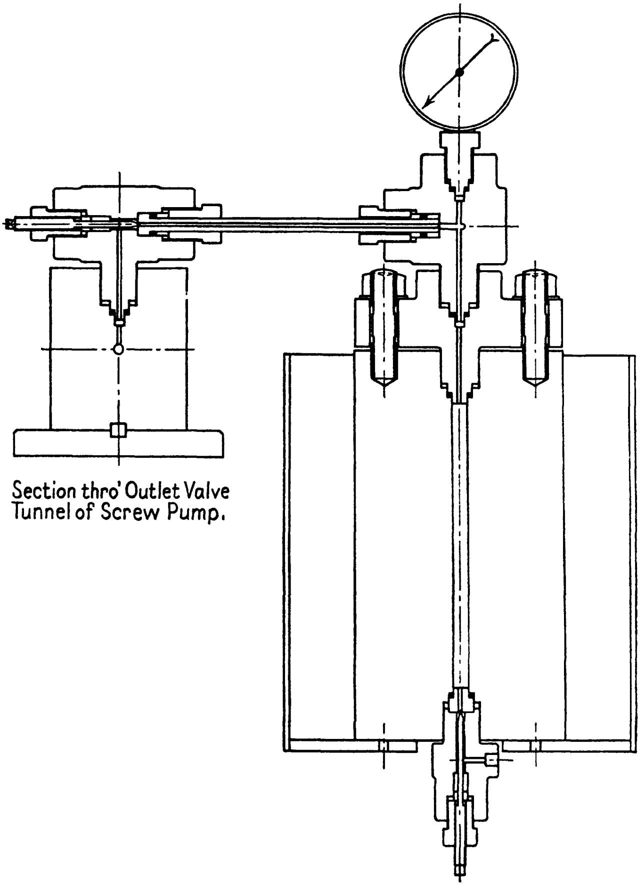

FIG. 197.—Chemical Research Laboratory 3000 atm. autoclave.

A pressure gauge (range 0-5000 atms.) is fitted to the top of the autoclave.

Compression of gas and liquids for this autoclave is carried out by means of a screw-driven plunger pump, $\frac{1}{2}$-in. diameter and 8-in. stroke (see Chap. II.). This pump, which is fitted with hand operated valves, is connected to the autoclave cover tee-piece by means of a pipe $\frac{7}{8}$-in. outside diameter and $\frac{1}{8}$-in. bore. The joints of this pipe are designed on the principle of Bridgman's "unsupported area," which was fully described in Chapter II. The joints of the pump and pipe line are made on magnolia white metal rings.

The whole of the pressure resisting parts of this apparatus were made from nickel-chrome-molybdenum steel of the following composition :—

C	Si	S	P	Mn	Cr	Ni	Mo
0·29	0·31	0·016	0·030	0·57	0·64	2·40	0·51

Test pieces were taken from the various parts and gave the following results :—

Yield. Tons/sq. in.	Ult. Tensile. Tons/sq. in.	Elon. on 2 in. Per cent.	Red of Area. Per cent.	Izod. Ft.-lbs.
1. PUMP BODY.				
Transverse tests taken near the bore.				
44·5	55·5	20	54·8	64, 71, 68
45·0	55·0	22	58·0	69, 68, 70
2. AUTOCLAVE BODY.				
Transverse tests taken near the bore.				
46	56·3	19	49·6	55, 52, 55
46	56·4	19	48·4	60, 58, 56
3. VALVES AND TEE-PIECES.				
Transverse tests.				
45	55·6	21	53·6	66, 66, 62

These forgings were supplied by Hadfields Ltd., and the whole of the machining except the long holes was carried out in the C.R.L. engineering shops. The long holes were bored by B.S.A. Ltd. in their Small Arms Department.

The valve spindles are made from V30 Vibrac steel, with special high carbon oil hardening tool steel points. All valve spindles are packed with leather packing rings, soaked in tallow. These valves were fully described in Chapter VI.

12,000 *Atm. Autoclave.*

An autoclave and accessories for 12,000 atms. recently built at the I.C.I. Laboratories at Northwich is shown in Figs. 198 and

199. I am indebted to the Editor of *Engineering* and the officer in charge at the I.C.I. Laboratories, Northwich, for permission to reproduce this description and illustration.

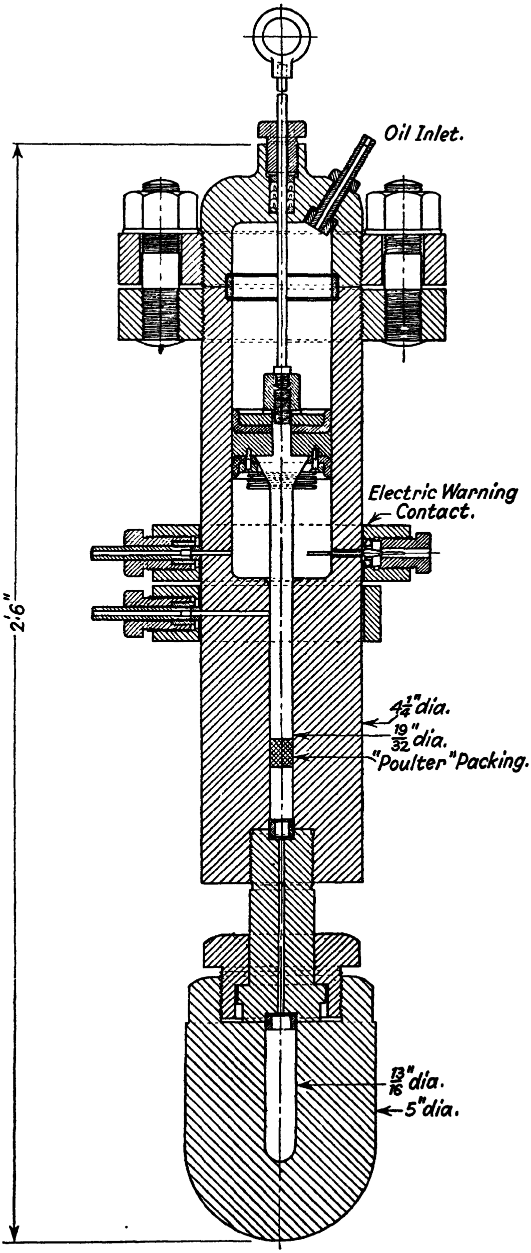

FIG. 198.—Details of I.C.I. 12,000 atm. autoclave.

The apparatus shown in section in Fig. 198 was made from Vibrac * steel, and was hardened and tempered to give a tensile strength of 70-75 tons per sq. in. before machining. The autofrettage process was applied in three stages and the intervening heat treatments were carried out at from 350 to 400° C. It consists, as shown, of a reaction vessel $\frac{13}{16}$-in. diameter, in which the substances to be examined are enclosed in small glass fittings sealed by mercury. The reaction vessel is coupled through a connecting piece to the large cylinder C, which is a hydraulic intensifier with an effective ratio of about 20 to 1. The high-pressure piston ($\frac{19}{32}$-in. diameter) which works in this cylinder is of hardened steel ground to a good sliding fit in the bore, and is connected at its upper end to a low-pressure piston. The latter is provided with the usual hydraulic cup leathers, but the packing of the high-pressure piston consists simply of a solid rubber plug which is initially of slightly larger diameter than the bore. This device, which was described by Poulter in the *Physical Review*, Vol. 40, p. 860 (1932), has proved quite effective in service. (See Chaps. II. and IV. for description of Poulter's technique.) An indicating stem F passes out through the cover G of the intensifier through a gland fitted with S.E.A. rings. As will be seen, the cover is secured to the body of the intensifier by screwed-on flanges held together by studs and nuts.

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* Ni-Cr-Mo Steel (English Steel Corporation).

To avoid the weakening of the body by cutting screw threads, etc., two straps are provided to hold the radial connections, this feature being due to Dr. A. Michels of Amsterdam. The upper strap carries a pressure connection used for withdrawing the piston in case it should stick, and also an insulated rod which makes contact with a spring on the under side of the low-pressure piston, and thereby completes an electric circuit which rings a warning bell and thus indicates that the piston is near the bottom of its stroke. The lower strap enables a pressure lead to be inserted through a port uncovered by the piston in its highest position, so that an initial pressure can be applied to the reaction vessel ; this, however, is only necessary when dealing with very compressible materials.

The joints on the small connections are made with hardened steel rings having spherical surfaces and known as " lens " rings ; the rings are held tightly by the axial pressure produced by the screw plugs. The large joint between the cover and the body of the intensifier and the two joints on the high-pressure side are of a novel form devised in the firm's own laboratories, and the subject of a British patent application. The joint, it will be seen, consists simply of a ring, usually made of hardened steel, having an outer surface of wave form ; the rings are thus usually referred to as " wave rings " (Fig. 200). The rings are made an interference fit in parallel-sided sockets formed in each of the two parts to be joined, and the joint thus made is self-tightening up to the highest pressure used. Since the actual contact pressure is radial, no initial axial pressure is required to keep the joint tight, the usual practice, in fact, being to slack off the nuts or plugs, so that initially they are no more than finger tight. The necessary interference is very small, being of the order of one part in 10,000 so that the rings can usually be forced into the sockets by a few light taps with a wooden mallet. When the rings are made of appreciably harder material than that in which the sockets are formed, the joints can be made and broken a great many times without damage, but where the joint is of a more or less permanent nature, a mild-steel ring may be employed. A ring of this material, we understand, undergoes considerable distortion in service without affecting the tightness of the joint.

The general arrangement of the apparatus is shown in Fig. 199. A thermostatically-controlled tank, working at temperatures up to about 200° C., is carried on a platform which can be raised to immerse the reaction vessel or lowered out of the way by means of a small winch. The low-pressure side of the intensifier is supplied with oil from a small hydraulic hand pump. The liquid below the high-pressure piston is usually a light lubricating oil, but for work requiring the highest pressures at room, or lower, temperature, this oil is liable to solidify, and kerosene is used instead. As will be clear from Fig. 199, the whole apparatus is suspended from two rolled steel channels in a small brick cubicle. The overall height of the intensifier and reaction vessel, assembled complete, is 2 ft. 6 ins. The intensifier cylinder is $4\frac{1}{4}$-in. external diameter with a bore $\frac{19}{32}$-in. in diameter in the high-pressure part, and the reaction vessel has a bore $\frac{13}{16}$-in. in diameter, with a parallel length of $3\frac{1}{4}$ ins. The complete apparatus weighs 165 lbs. in working order.

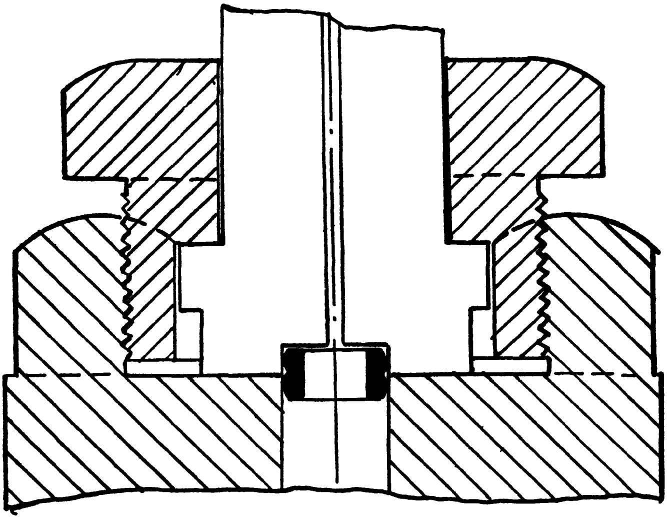

FIG. 200.—Enlarged view of I.C.I. wave-ring joint for high pressures.

Chemical Reactions carried out in Autoclaves.

The following examples of typical autoclave reactions are included to show the remarkable way in which high pressure is entering into many phases of chemical manufacture. I have not included any reference to the literature in connection with dyestuffs, as the use of pressure in this specialised subject is well known, and information thereon is available in standard text-books. Numerous examples of other types of autoclave reactions will also be found in books such as Carlton Ellis's " Hydrogenation of Organic Substances," or Stanley Green's " Industrial Catalysis."

I have also included a selection of examples on the subject from the Patent literature, to show the trend of development in this branch of industrial chemistry.

The following autoclave operations will illustrate the wide variety of work to which these appliances have been put at the Chemical Research Laboratory.

(1) Hydrogenation.

2-nitrofluorenone is reduced successively to 2-aminofluorenone, 2-aminofluorenol and 2-aminofluorene. This process is carried out in alcoholic solution, using 1 per cent. of platinic oxide as a catalyst. The catalyst is recovered at the conclusion of the work. This is a development of the catalytic reduction process recently employed by Bennett and Noyes (*J. Amer. Chem. Soc.*, 1930, **52**, 3438). The following table gives a summary of the work in this connection carried out at the Chemical Research Laboratory :—

Temp. °C.	Pressure Atm.	Nitro Compound.	Amino-Fluorenone. Per Cent.	Amino-Fluorenol. Per Cent.	Amino-Fluorene. Per Cent.
45	5-2	Nitrofluorenone	80-85	10	—
25-30	26-20	„	60	30	Small amount
45	38-30	„	30	60	„
30	8-5	„	0	75	„
40-45	20-12	Nitrofluorene	—	—	80

This work has been published in *J.C.S.*, 1931, p. 620.

The autoclaves at Teddington have also been employed for the study of the hydrogenation of the constituents of low temperature tar. A sample of this tar, topped to 200° C., was hydrogenated under 120-200 atms. pressure of hydrogen in the presence of molybdic acid and sulphur for six hours. Hydrogenation appeared to commence at a temperature of 350° C., but further changes, including cracking, occur at temperatures just over 400° C. Distillation of the products formed at the latter temperatures yields 28 per cent. light oil, b.p.

up to 200° C., 50 per cent. medium oil, b.p. 200-300° C., and a residue of 17 per cent. boiling over 300° C.

The wax of low temperature tar was also hydrogenated under similar conditions. The wax melting at 50° C. yielded a mobile, colourless oil from which stable water-white distillates, representing 35 per cent. of the wax and boiling up to 200° C., were obtained. The residue over 200° C. is an oil solidifying at 0° C. The resinoids of low temperature tar also yielded a high proportion of mobile oil when hydrogenated under the above conditions (*J.S.C.I.*, 1932, **51**, 80T).

(2) Dehydrogenation.

An example of this is the conversion of pyridine into 2 : 2′-dipyridyl by the action of anhydrous ferric chloride. This process was originally carried out by Hein and Retter in sealed glass tubes, using 13 grams of ferric chloride and 70 grams of pyridine, and the sole product was 2 : 2′-dipyridyl. By working with 8 litres of pyridine and a corresponding amount of ferric chloride, in the large 12-litre autoclave described earlier in this chapter, about twenty products were obtained from this reaction at the Chemical Research Laboratory. Five of the six possible dipyridyls have been obtained, a whole range of monocyclic pyridine derivatives and a new triamine, namely, 2 : 2′ : 2″-tripyridyl.

The above reaction was carried out at temperatures of 325-335° C., and the pressure developed in the autoclave was between 45-55 atms. This work was published in the *Journal of Chemical Society* (Morgan and Burstall, *J.C.S.*, 1932, 20).

(3) Amination.

Many experiments have been carried out at Teddington on the amination of aliphatic alcohols and phenols. The high-pressure autoclaves were used for this purpose. In one experiment, ethyl alcohol and ammonium chloride were heated together for six hours in an autoclave at a temperature of 280° C. The pressure was of the order of 100 atms. The resultant mixture was distilled to remove excess of alcohol, water and any neutral oils. The bases are set free by caustic soda, distilled and fractionated over solid caustic soda, using a Dufton column. In this way quite good fractionation is obtained. The three bases produced are ethylamine, b.p. 19° C., diethylamine, b.p. 56° C., and triethylamine, b.p. 88° C. Small quantities of higher bases of a cyclic character are also produced. As an alternative ammonium bromide may be used in place of ammonium chloride, in which case the yield of triethylamine is increased, and the reaction is of a less corrosive character. (See G. T. Morgan, "The Autoclave in Organic Synthesis," *Chemical Age*, 1932, **27**, 572.)

(4) Carboxylation.

An interesting example of carboxylation in an autoclave involving the use of carbon dioxide under pressure is given in English Patent No. 307,223 (I.G. Farbenindustrie, A.G.), which is briefly as follows :—

If benzene is heated with aluminium chloride in an autoclave to a temperature of 100° C., or so, under a pressure of carbon dioxide of 50-60 atms., quite an appreciable yield of benzoic acid is produced, along with a certain amount of benzophenone. Toluene in similar circumstances yields *p*-toluic acid and di-*p*-tolyl ketone. The same process can be adopted for use with chlorobenzene and *m*-xylene.

This process has been developed at Teddington to reactions involving aromatic amines. For example, aniline and carbon dioxide in presence of aluminium chloride at 100° C., and a pressure of 70 atms., yields diphenylurea. A similar reaction carried out with dimethylaniline furnishes *p*-dimethylaminobenzoic acid, and also the well-known Michler's ketone—tetramethyl-*pp*-diaminobenzophenone.

Recently at Teddington there has been carried out a study of the reaction between phenol and its homologues when heated with ammonium chloride at temperatures of 300-350° C., which involves a pressure of 50-100 atms. When phenol is used, aniline is produced with a small proportion of diphenylamine. A very interesting case is that of *m*-cresol under these conditions, when a good yield of *m*-toluidine is obtained.

In the case of *sym.*-xylenol, when this is heated in an autoclave at 320° C. with ammonium chloride, two products are obtained in practically equal amounts. One is *sym.*-xylidine and the other is a new base discovered at Teddington in the course of this work. This is *sym.*-dixylylamine. (See Morgan and Pratt, *J.S.C.I.*, 1932, **51**, 283T.)

An interesting reaction involving the use of autoclaves is that of the manufacture of urea from carbon dioxide and ammonia. A large experimental plant for this purpose has been described by Krase, Gaddy and Clark (*Ind. Eng. Chem.*, 1930, **22**, 288). The flow sheet (Fig. 201) gives details of the plant layout. The plant was built at the Fixed Nitrogen Laboratories of the Bureau of Chemistry and Soils, Washington, D.C., U.S.A.

The operation is briefly as follows :—

Liquid ammonia and carbon dioxide are delivered to the plant in the ratio $2NH_3 : CO_2$. Both liquids enter the urea autoclave, where reaction and conversion into urea takes place. After leaving the autoclave, the contents, which now consist of a liquid mixture of urea, water and carbon dioxide compounds of ammonia, enter a still where the dissociation of the ammonium compounds is accomplished by the application of heat. The urea leaves the still in aqueous solution. The ammonia and carbon dioxide leave the still in gaseous form, and enter a regenerator where the ammonia is absorbed in aqueous solution. The carbon dioxide is discharged from the regenerator into the compression system.

The urea autoclave was constructed from a small naval gun, and was 4·5-in. internal diameter and 7 ft. long. At the thinnest part of the wall the thickness was 1¼ ins.

The interior was lined with an 0·5-in. thick lead liner cast in place. The autoclave was fitted with a steam jacket which was welded on.

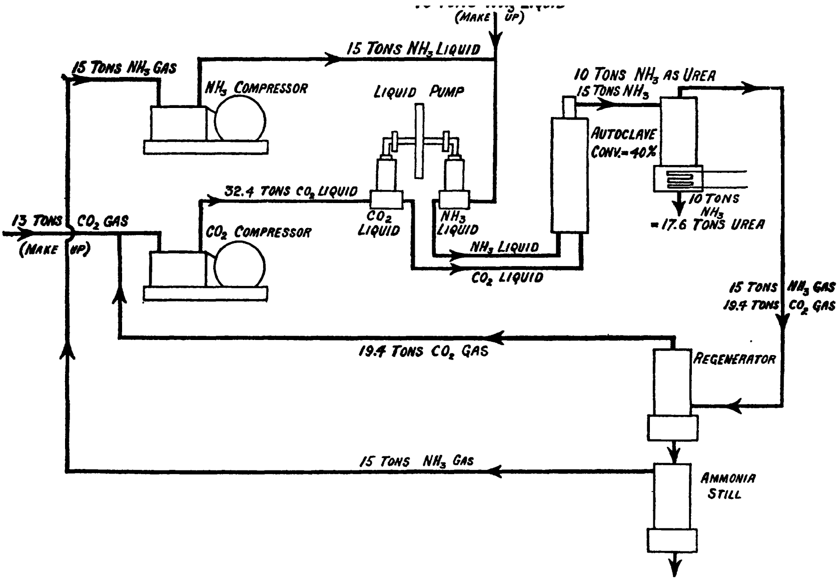

FIG. 201.—Layout of urea plant.

The internal volume of the autoclave was just under 4 gallons. The operating conditions were usually a pressure of 100-110 atms., a steam pressure in the jacket of 60 lbs. (gauge) or 153° C., and input per hour of 10·4 and 13·5 lbs. of ammonia and carbon dioxide respectively. Conversion of the reactants to urea was of the order of 35-37 per cent.

Serious operating troubles arose with this plant, owing to severe corrosion of the autoclave equipment. Accordingly Thompson, Krase and Clark carried out an investigation on this subject in an endeavour to find suitable materials (*Ind. Eng. Chem.*, 1930, **22**, 734). They found that a high chromium-nickel-silicon alloy, known in

U.S.A. as Rezistal 4 (0·23 C, 18 per cent. Cr, 22·5 per cent. Ni and 2·9 per cent. Si), was probably the best all-round metal for the construction of bombs, heads, etc. The high silicon irons (14 per cent. Si) were found to be resistant, but, of course, these alloys are brittle and unmachinable.

A later paper by Clark and Gaddy (*Ind. Eng. Chem.*, 1930, **22**, 1084) gives further details of the urea plant of the Fixed Nitrogen Laboratory, which in the interval had been successfully operated at rates of production of 175 lbs. of urea per day.

They found that the overall autoclave reaction was strongly exothermic, and confirmed that the high silicon-chrome-nickel steels are best for the reaction vessel parts in contact with the reacting mass of ammonia, carbon dioxide, urea, etc.

Recent English Patents dealing with Chemical Reactions requiring Pressure Plant of the Autoclave type.

385,004. *Facilitating chemical reaction by irradiation.*

I.G. Farbenindustrie, A.G. June, 1931.

In a process for the polymerisation of vinyl halides by heating in closed vessels in the presence of peroxide catalysts in the absence of solvents, and, if desired, in the presence of organic acid anhydrides, the process being interrupted when a considerable amount, say one-half, of the momomeric vinyl halide is still present, the polymerisation is considerably accelerated if the vinyl halide is subjected to a preliminary irradiation, e.g. by passing through a quartz tube illuminated by a mercury vapour lamp prior to admission into the autoclave.

385,625. *Catalytic hydrogenation-alcohols.*

Du Pont de Nemours & Co. April 2nd, 1931.

Esters of aliphatic carboxylic acids are converted into alcohols by hydrogenation under pressure at a temperature above 200° C., and preferably 300-400° C., using a composite catalyst. The catalyst may contain any hydrogenating metal or oxide, such as copper, tin, cadmium, lead, iron or nickel with or without promoters such as oxides of manganese, zinc, magnesium or chromium. According to a typical example, ethyl acetate is converted to ethyl alcohol by hydrogenation at 370° C., and 3200 lbs./sq. in. pressure, using as catalyst a mixed chromite of cadmium, copper and zinc.

348,248. *Catalytic hydrogenation.*

I.G. Farbenindustrie. February, 1930.

In the production of 1 : 3-butylene glycol from crude aldol by catalytic hydrogenation, the first stage of the reaction is carried out at temperatures of 30-80° C. Suitable catalysts are the metals of first and eighth groups of the periodic system alone or in admixture. According to an example, the reaction is carried out in a vertical column under a pressure of 90 atms. The column is charged with a catalyst comprising finely divided metallic copper deposited on silica gel. A mixture of crude aldol and ethyl alcohol acidified with acetic acid to p_H 4·8 is introduced at the top of the column where it is heated to about 80° C. Hydrogen also entering at the top of the column forces the liquor downwards over the surfaces of the catalyst and the reaction product is withdrawn from the foot of the column after being heated to about 120° C.

311,671. *Catalytic production of hydrogenated organic compounds.*

I.G. Farbenindustrie, A.G. February, 1928.

Aldol is reduced to 1 : 3-butylene glycol by passing it in the liquid or dissolved state, together with hydrogen or gases containing the same over a hydrogenating catalyst, such as nickel, copper, etc., at temperatures above 50° C., and hydrogen pressures of 20-100 atms.

352,537. *Catalytic processes.*

I.G. Farbenindustrie, A.G. April, 1930.

Products consisting mainly of higher aliphatic alcohols are obtained by heating the products resulting from the destructive oxidation of difficultly volatile hydrocarbons in the liquid state with gaseous oxidants containing free oxygen in the presence of hydrogen and a hydrogenation catalyst at a pressure greater than atmospheric. Applications of the product include preparation of ointments, esters and sulphonation products for use as cleaning, wetting and emulsifying agents.

According to examples an oxidation product containing free carboxylic acids obtained by blowing paraffin oil at 160° C., with air in the presence of manganese naphthenate is heated with hydrogen at 180° C. and 50 atms. pressure in presence of metal deposited on kieselguhr. The saponifiable constituents are hydrolysed with caustic soda and separated, leaving a mixture of higher alcohols.

354,196. *Hydrogenation of aldoses.*

I.G. Farbenindustrie, A.G.

Polyhydric alcohols are obtained by treating aldoses of natural origin, such as glucose, with hydrogen in the presence of water, a base metal reducing catalyst and a quantity of alkali to produce a hydrogen-ion concentration of p_H 7-12. Suitable catalysts are nickel, copper, cobalt and their alloys and oxides which may be activated by addition of difficultly reducible metal oxides, e.g. oxides of chromium, molybdenum, etc.

The reaction may be carried out at temperatures between 30-160° C., and pressures up to 90 atms.

357,152. *Hydrogenation of aliphatic cyanhydrins.*

Dreyfus, H. June, 1930.

Hydroxy aliphatic amines are manufactured by hydrogenation of cyanhydrins in the presence of hydrogenation catalysts, such as nickel, copper, platinum, palladium, cobalt and iron. The hydrogenation may be carried out at atmospheric or raised pressure.

367,003. *Emulsions—Catalytic hydrogenation.*

I.G. Farbenindustrie. November, 1930.

Alcohols of high molecular weight suitable for the preparation of ointments, creams and polishing compositions are made by reduction with hydrogen, and a catalyst, of the oxidation products of liquid or solid non-aromatic hydrocarbons, such as paraffin wax or paraffin oil and the alcohols are then extracted with a water soluble aliphatic alcohol, such as methanol in the presence of water.

An example is given :—

(1) The oxidation product of hard paraffin is treated with caustic soda to remove the acids and the unsaponifiable portion is separated from the greater part of the unattacked hard paraffin by centrifuging, and is hydrogenated at 250° C., with a nickel catalyst at 50 atms. pressure. The product is stirred with methanol containing 4 per cent. of water ; on standing the upper layer contains about 60 per cent. of the alcohols, a second extraction recovering the rest of the alcohols.

378,943. *Hydrogenised organic compounds.*

E. B. Maxted. May, 1931.

The hydrogenation of unsaturated organic compounds in the liquid state is effected with catalysts consisting of a mixture of chromium oxide and zinc oxide, or a mixture of chromium and zinc oxide prepared in a compact form by the oxidation of an alloy of the two metals. Examples are (1) Unsaturated oil of the glyceride type is hydrogenated at 150° C., and 200 atms. pressure, using a chromium oxide-copper oxide catalyst obtained by anodic oxidation of a copper-chromium alloy. (2) Acetone is converted into isopropyl alcohol at 150° C., and 150 atms. with the same catalyst.

371,051. *Catalytic hydrogenation of crotonaldehyde.*

Horsley and I.C.I. January, 1931.

Butyraldehyde is obtained by treating crotonaldehyde in the liquid phase with hydrogen, preferably in counter current under increased pressure in presence of a catalyst comprising nickel and chromium or their compounds. A suitable catalyst is obtained by the co-precipitation of nickel and chromium oxides on asbestos fibre from an aqueous solution of nickel nitrate and chromium sulphate by means of sodium hydroxide and subsequently drying and reducing with hydrogen.

362,457. *Catalytic hydrogenation of mesityl oxide.*

British Industrial Solvents Ltd. September, 1930.

Mesityl oxide is hydrogenated in the presence of a nickel catalyst under pressure substantially greater than atmospheric, and at temperatures of 140° C. or less, to produce 2-methylpentanon or isobutyl ketone, or between 170-210° C., to produce the corresponding alcohol. According to examples, the ketone is obtained at 8-10 atms., while to produce the alcohol pressure is increased to 20-30 atms.

369,690. *Catalytic hydrogenation of fatty acid nitriles.*

I.G. Farbenindustrie. January, 1931.

Saturated fatty acid nitriles are obtained by hydrogenation of unsaturated nitriles under mild conditions of working, using a copper catalyst; suitable temperatures are 50-200° C. for increased pressure, and 100-400° C. for ordinary pressure. Examples are given of the conversion of acrylic nitrile to propionic nitrile and of crotonic to butyric nitrile.

375,972. *Hydrogenated organic compounds.*

I.G. Farbenindustrie. June, 1931.

Rubber materials, such as crepe rubber, balata, gutta-percha and polymerisation products of butadiene, are partially or wholly hydrogenated in solvents such as cyclohexane. Temperatures between 240° and 350° C. are used, depending upon the material, and pressures of 30-200 atms. are suitable. Nickel, cobalt, platinum catalysts are mentioned.

263,862. *Catalytic production of hydrogenated organic compounds.*

H. Staudinger. December, 1925.

Caoutchouc is converted by heating into a cyclic compound and this compound is transformed into a fully saturated compound by treatment with hydrogen under pressure, at a temperature above 200° C., in the presence of an hydrogenation catalyst, preferably a metal of the eighth series of the periodic system.

An example is: Cyclocaoutchouc, obtained by heating caoutchouc, is triturated with platinum or nickel and heated in a rotary autoclave at 50-80 atms. pressure of hydrogen for 20-30 hrs. at 270° C. The mass is extracted with benzene, filtered and the hydrocyclocaoutchouc is obtained by distilling off the benzene or by precipitation with alcohol.

355,945. *Catalytic hydrogenation of indiarubber.*

Felten and Guilleaume Carlswerk, A.G. September, 1929.

Hydrocaoutchouc is prepared by treating caoutchouc with hydrogen in an autoclave at temperatures between 200-300° C., in the presence of catalysts such as platinum, palladium or nickel and under a pressure of 30-60 atms.

362,049. *Catalytic hydrogenation of caoutchouc.*

Felten and Guilleaume Carlswerk, A.G., Mulheim, Germany.

Hydrogenated caoutchouc is prepared by treating ordinary natural or synthetic caoutchouc with hydrogen in an autoclave in the presence of catalysts such as nickel, platinum or palladium at temperatures between 200 and 300° C. and 30-60 atms.

290,175. *Hydrogenation of organic compounds.*

I.G. Farbenindustrie, A.G. May, 1927.

The homologues of aniline and mono-amino compounds of aromatic hydrocarbons containing condensed benzene nuclei are hydrogenated by treatment in the liquid phase with hydrogen under pressure at an elevated temperature in the presence of a catalyst of the nickel group. Examples are given of the hydrogenation of *o*-, *m*- and *p*-toluidines and *p*-xylidine to the corresponding hexahydro compounds.

366,244. *Catalytic hydrogenation.*

Schering-Kahlbaum, Akt.-Ges. January, 1930.

Hydroaromatic alcohols containing a preponderance of the *trans*-form are prepared by the catalytic hydrogenation of the alkali metal salts of aromatic hydroxy compounds in aqueous or alcoholic solution. An example is the conversion of sodium-*p*-cresolate into *trans*-4-methyl*cyclo*hexanol by treatment with hydrogen at elevated temperatures in the presence of nickel.

381,954. *Catalytic hydrogenation.*

I.G. Farbenindustrie, A.G. July, 1931.

4-Phenyl*cyclo*hexylamine is obtained by hydrogenating 4-aminodiphenyl with hydrogen in the presence of a cobalt catalyst.

361,493. *Catalytic reduction of nitro compounds.*

C. Mannich. 1930.

The *p*-nitrobenzoic acid esters of 3-dimethylamino-2-dimethylpropane-1-ol, 3-diethylamino-2-dimethylpropane-1-ol, and 3-dimethylamino-2-isopropylpropane-1-ol are reduced to the corresponding *p*-aminobenzoic acid ester by treatment with hydrogen under pressure in the presence of palladium chloride.

343,072. *Catalytic production of amino compounds.*

I.G. Farbenindustrie. November, 1929.

5-Amino-7-chloro-2-oxobenzimidiazole-2 : 3-dihydride is prepared by the catalytic reduction of the corresponding 5-nitro compound.

343,744. *Catalytic production of amino compounds.*

I.G. Farbenindustrie, A.G. February, 1930.

o-Diacyldiamino-aminobenzenes are prepared by the catalytic reduction of *o*-diacyldiamino-nitrobenzenes. A nickel catalyst is used with hydrogen under pressure.

365,640. *Reduction of nitro compounds.*

I.G. Farbenindustrie. October, 1930.

1-Diethylaminoethoxy-3 : 4-diaminobenzene is prepared by treatment of 1-diethylaminoethoxy-3-nitro-4-aminobenzene with hydrogen in the presence of palladium.

297,212. *Catalytic production of amino compounds from nitro compounds and hydrogen.*

I.G. Farbenindustrie, A.G.

The catalytic reduction of nitro compounds with hydrogen to produce aromatic amines is carried out at pressures of at least 20 atms., and in presence of sulphur compounds which partly poison the catalyst, and so prevent the formation of undesirable by-products. According to an example, 300 parts of nitrobenzene are stirred with 100 parts of Swedish spongy iron under a pressure of 140 atms. of hydrogen ; 220 parts of aniline are obtained.

340,682. *Catalytic hydrogenation and dehydrogenation.*

Schering-Kahlbaum, A.G. October, 1929.

Alkylphenols are prepared by heating dihydroxydiphenylmethane compounds with cyclic alcohols in equimolecular proportions at a temperature of about 220° C., in the presence of an hydrogenation catalyst.

254,753. *Catalytic preparation of hydrogenated organic compounds.*

Chemische Fabrik Auf Actien. July, 1925.

Alkyl phenols and *cyclo*hexanols are obtained by the catalytic hydrogenation of the condensation products of a ketone with a phenol. Thus *p*-dihydroxydiphenyldimethylmethane yields either a mixture of *p*-*iso*propylphenol and phenol or a mixture of *p*-*iso*propyl-*cyclo*hexanol and *cyclo*hexanol. The production of the alkyl phenols is effected with the aid of a catalyst comprising nickel or other hydrogenation catalyst mixed with bismuth. The use of pressure is advantageous.

376,479. *Hydrogenised organic compounds.*

I.G. Farbenindustric, A.G. June, 1931.

The ketone obtained by condensing tetrahydronaphthalene with acetyl chloride by the Friedel Crafts reaction is reduced to the corresponding alcohol by hydrogen at a raised pressure with a nickel catalyst.

227,481. *Catalytic production of amino compounds from nitro compounds and hydrogen.*

Poma, G., and Pellegrini, G. August, 1923.

α-nitronaphthalene is catalytically reduced to α-naphthylamine by heating it with agitation in an autoclave in the presence of water, a catalyst and hydrogen preferably under pressures of 4-5 atms.

276,571. *Hydrogenated organic compounds.*

Soc. of Chemical Industry in Basle. February, 1927.

ar-Tetrahydronaphthylamine derivatives are obtained by subjecting N-substituted naphthylamines to catalytic hydrogenation and the hydrogenated naphthylamines themselves may be obtained by using an acetyl derivative as the starting material, and subsequently saponifying. Hydrogen is used under pressure in the presence of a nickel catalyst.

340,585. *Destructive hydrogenation.*

I.G. Farbenindustrie, A.G. September, 1929.

Carbazole is recovered from tar fractions containing it by treating the initial material with hydrogen at temperatures between 300-550° C., and under pressure preferably in the presence of catalysts. In an example, a mixture of anthracene residues and anthracene oil is heated with hydrogen under a pressure of 200 atms. at 440° C., in the presence of a catalyst containing molybdenum, chromium and manganese.

250,380. *Hydrogenated organic compounds.*

Howards & Sons and J. W. Blagden. March, 1925.

Cinchona alkaloids or their derivatives are hydrogenated to the hexahydro compounds by treatment with hydrogen in the presence of a catalyst (such as nickel, iron, cobalt or copper) at a temperature of about 30° C.

342,010. *Catalytic hydrogenation and dehydrogenation.*

Schering-Kahlbaum, A.G. November, 1929.

Pyridine, quinoline and their homologues are hydrogenated by interaction in the presence of a hydrogenation catalyst with such hydrogenated compounds, e.g. *cyclo*hexanol and tetrahydronaphthalene, as can readily be dehydrogenated under the reaction conditions. According to the examples, piperidine and *cyclo*hexanone are obtained by heating pyridine (1 mol.) with *cyclo*hexanol (3 mols.) in the presence of nickel at 210-230° C.; pyridine is heated with hydrogen under pressure in the presence of nickel and about 10 per cent. of phenol; hydrogenation of phenol thereby takes place, and on raising the temperature to 160-180° C., piperidine is produced.

378,300. *Hydrogenating oils.*

I.G. Farbenindustrie, A.G. December, 1931.

Hydrogenated products devoid of unpleasant odour and suitable as vehicles for insecticides are obtained by hydrogenating a lignite tar oil at 390° C., and a pressure of 200 atms. in the presence of a tungsten sulphide catalyst, and by hydrogenating an oil obtained from high temperature carbonisation coal tar at 350° C., and 200 atms. in the presence of a catalyst comprising cobalt and molybdenum sulphides, and further treating the product with hydrogen at 300° C., and 100 atms. in the presence of a nickel catalyst.

296,006. *Hydrogenated organic compounds, Catalytic production of.*

Soc. of Chemical Industry in Basle. August 22, 1927.

The hydrogenation of arylamino alkyl ketones to the corresponding carbinols is effected in alkaline solution. Nickel or metals of the platinum group may be employed as catalysts and the hydrogen should be under pressure.

309,865. *Catalysts.*

Schering-Kahlbaum, A.G. April, 1928.

A catalyst for the preparation of *p*-*iso*propylphenol from di-(4-hydroxyphenyl)-dimethylmethane and thymol from di-(4-methyl-6-hydroxyphenyl)-dimethylmethane, by treatment with hydrogen under pressure, comprises a mixture of the carbonates or hydroxides of nickel and copper together with small quantities of those of cobalt and iron.

341,997. *Catalytic hydrogenation.*

Schering-Kahlbaum, A.G. October, 1929.

Menthenes are prepared by the partial hydrogenation of menthadienes containing a double bond outside the ring, which is effected by employing nickel as the catalyst at the low temperature of 40-80° C. Examples are given of the partial hydrogenation of β-terpinene to Δ^3-menthene, sylvestrene to Δ^1-*m*-menthene, etc., and in each case the hydrogen is employed under pressure.

285,394. *Hydrogenated organic compounds, Catalytic production of.*

Rheinische Kampfer Fabrik. Ges. February, 1927.

Thymol, menthone or *iso*menthone is hydrogenated under pressure in the presence of a nickel catalyst. The liquid menthol mixtures obtained thereby are shown to consist of inactive neo-menthol, an unknown inactive neo*iso*menthol and some remaining inactive menthol. Inactive neo*iso*menthol is produced by the hydrogenation of thymol and *iso*menthone preferably at temperatures below 160° C.

279,401. *Hydrogenated organic compounds.*

I.G. Farbenindustrie, A.G. October, 1926.

2-Aminoanthrahydroquinone-9 : 10-diethers are obtained by reducing 2-amino or 2-acylaminoanthraquinones, alkylating the resulting leuco compounds, and in the case of the acylamino compounds splitting off the acyl residue. Thus, for example, 2-acetaminoanthraquinone is reduced in alcoholic solution in presence of nickel by means of hydrogen under pressure.

282,410. *Preparation of catalytic agents.*

I.G. Farbenindustrie, A.G. December, 1926.

Catalysts consisting of nickel, cobalt, copper or mixtures thereof are prepared by precipitating the metal from ammoniacal solution by means of hydrogen. The process is preferably carried out under pressure, and is facilitated by the initial presence of a catalytic metal. The preparation may be carried out in the presence or absence of a carrier such as kieselguhr.

364,134. *Catalytic agents.*

Fuchs and Querfurth. July, 1930.

Catalytic materials for the conversion of ethyl alcohol into higher alcohols by treatment with hydrogen compose an alkaline earth metal oxide, especially magnesia, activated by the presence of one or more oxides of the metals lead, silver, uranium, tungsten, cadmium, tin, chromium, manganese, zinc, iron, nickel, cobalt, copper and alkali metals. The catalytic mixture may be stabilised by addition of aluminium hydroxide, stannic acid, silver gel or wood charcoal.

365,214. *Catalytic agents.*

I.G. Farbenindustrie. October, 1930.

The hydrogenation catalysts employed for the production of amines by the treatment of carbonyl compounds with ammonia or amines in the presence of hydrogen comprised finely divided metals of the eighth periodic group which may be activated by the addition of metallic oxides or compounds furnishing the same. According to one of the examples nickel carbonate is soaked with chromic acid solution and reduced with hydrogen.

CHAPTER IX.

HIGH-PRESSURE CATALYTIC CIRCULATORY PLANTS.

It is now proposed to discuss the continuous type of pressure equipment, e.g. such as is used for the synthesis of methyl alcohol, the synthesis of ammonia, the hydrogenation of coal, crude oils, etc. Such plants are usually described as high-pressure catalytic circulatory plants, since in nearly all cases a catalyst is used to promote chemical change in a closed circulatory system.

Plants of the ammonia and methyl alcohol type, in which the reactants are gaseous, comprise a low-pressure gas storage system, such as the ordinary bell gas holder, a compressor for raising the gas pressure to that required in the synthesis plant, a catalyst tube with heating arrangements, a condenser to remove liquid product, such as methyl alcohol or ammonia from the system, and finally a high-pressure gas circulating pump to circulate the gases over the catalyst mass.

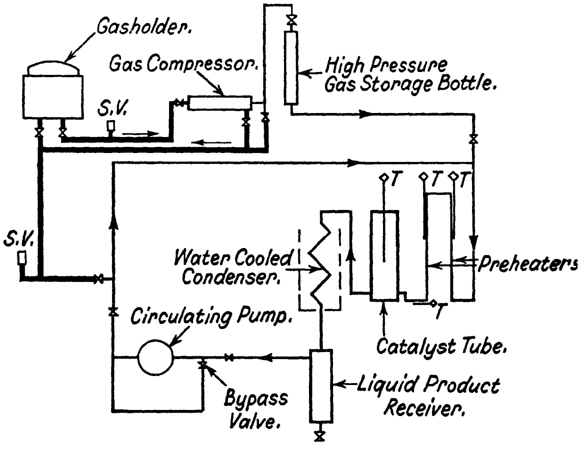

Fig. 202.—Layout of C.R.L. circulatory plants.

The following is a description of a plant for the study of catalytic reactions between carbon monoxide and hydrogen at high pressure, as designed and built and now in operation at the Chemical Research Laboratory. Referring to Fig. 202, the gasholder is of the wet bell type, with a maximum gas capacity of 500 cu. ft. (at N.T.P.).

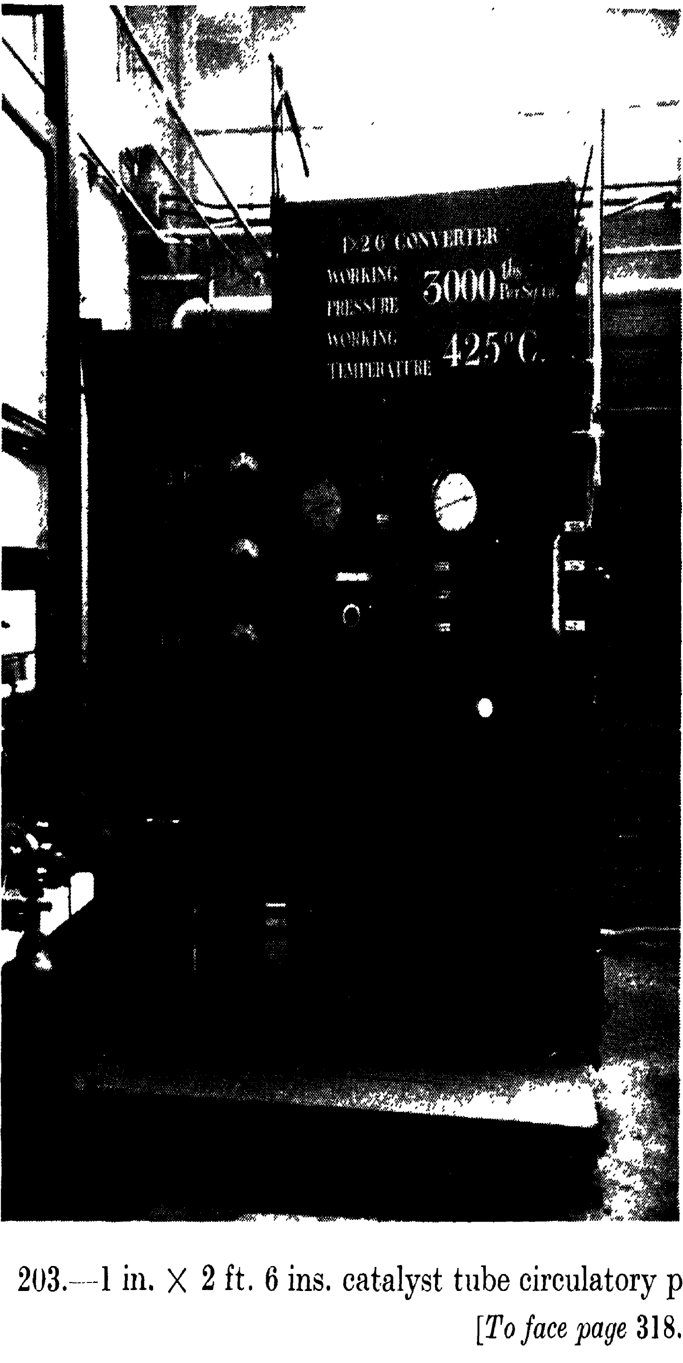

FIG. 203.—1 in. × 2 ft. 6 ins. catalyst tube circulatory plant.

[*To face page* 318.

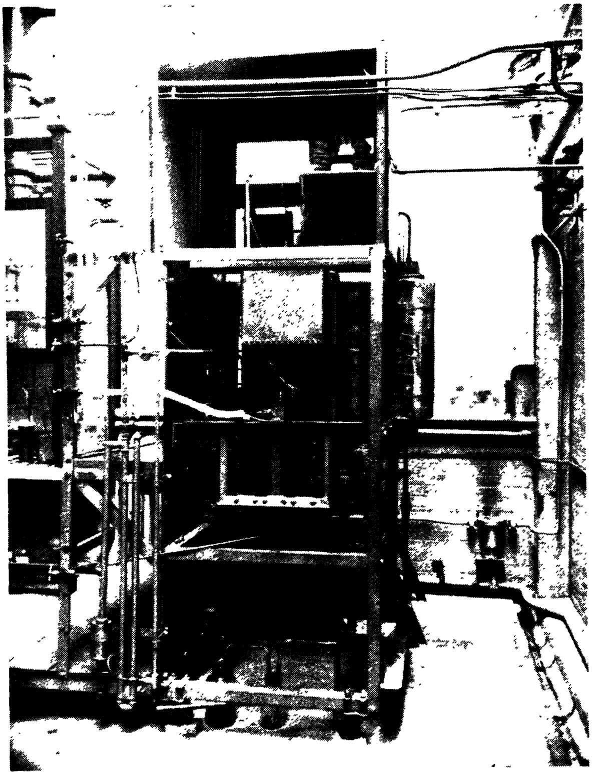

FIG. 204.—Side view of 1 in. × 2 ft. 6 ins. catalyst tube circulatory plant.

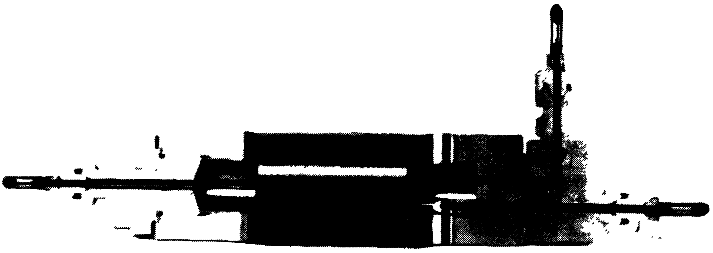

FIG. 207.—Photograph of partial section of high-pressure product receiver. 1 in. × 2 ft. 6 ins. catalyst tube circulatory plant.

[*See page* 321.

Assuming that it is desired to make methanol, the gasholder is filled with a mixture of carbon monoxide and hydrogen in the appropriate proportions. This gas is compressed by means of the gas compressor to 235 atms. and the high-pressure gas storage bottle is filled with the gas mixture at this pressure.

A four-stage Hofer compressor, similar to that described in Chapter II., is used for this purpose, and the storage bottle is that described in Chapter IV. (internal volume, 3 cu. ft.), page 163.

The catalyst tube of the circulatory plant is charged with the requisite amount of catalyst (zinc chromate or zinc oxide for example) and the whole circulatory system washed through with hydrogen to remove air. The high-pressure gas mixture from the storage bottle is then admitted to the system until the pressure reaches that desired (200 atms.) and the circulating pump is started up. The gas preheaters and the catalyst tubes are then slowly heated (electrically) until the desired reaction conditions are attained. This requires a catalyst temperature of 400° C. The methanol produced in the catalyst tube is condensed in the water-cooled condenser, and drawn off from time to time from the high-pressure liquid product receiver. The rate of circulation of the gas over the catalyst can be varied by adjustment of the by-pass valve between the delivery and suction sides of the circulating pump. Methods of measuring the rate of gas flow were given in Chapter II.

As the pressure in the circulatory plant falls (due to the formation of a liquid product from the reacting gases), fresh gas is added to make up the deficiency from the high-pressure gas storage bottle, which is maintained at a pressure a little higher than the circulatory plant by compression of more gas from the gasholder at intervals as desired.

The temperature of the preheaters, of the gas entering the catalyst tube and of the catalyst mass are all obtained by thermocouples marked " T " on the figure.

It will be noticed that there are two safety valves (S.V.) on the low-pressure gas lines to and from the gasholder. These fittings are most important when high-pressure gas is returned to a gasholder from a compressor, a storage bottle or a catalytic plant, in order to prevent dangerous overpressure if the gasholder maincocks (C.C.) are accidentally closed, or if it is forgotten to open them when returning high-pressure gas to the holder.

Two such high-pressure systems have been built at the Chemical Research Laboratory. A front view of the first is shown in Fig. 203. Nearly all the pressure parts are fitted behind a stout steel screen, and all valves and controls are arranged conveniently in a group at the front of the screen. The electrical resistances for the control of the heating of the gas preheaters and the catalyst tube, together with ammeters, are mounted to the left of the screen, in the centre of which are grouped the gas inlet valves to the circulatory system, the indicator for the various thermocouples and the pressure gauges. (These pressure gauges are now mounted behind the steel screens, to prevent personal injury should they happen to burst during an experiment.) On the right are the valves in connection with the circulating pump, and at the bottom right-hand corner is the valve from the high-pressure product receiver, which is drained at intervals of half an hour as a general rule.

A side view of this catalytic plant is shown in Fig. 204. The preheaters are at the back, and the catalyst tube (marked in chalk "Bomb") is to the right of the photograph. The tube leading from the top of the catalyst tube to the water-cooled condenser is clearly shown. The galvanised riveted tank contains the water-cooled condensing coil, which is a close spiral coil of copper tube. The high-pressure product receiver is immediately beneath this tank, and the pipe leading from the bottom of this receiver to the product release valve is quite clearly brought out.

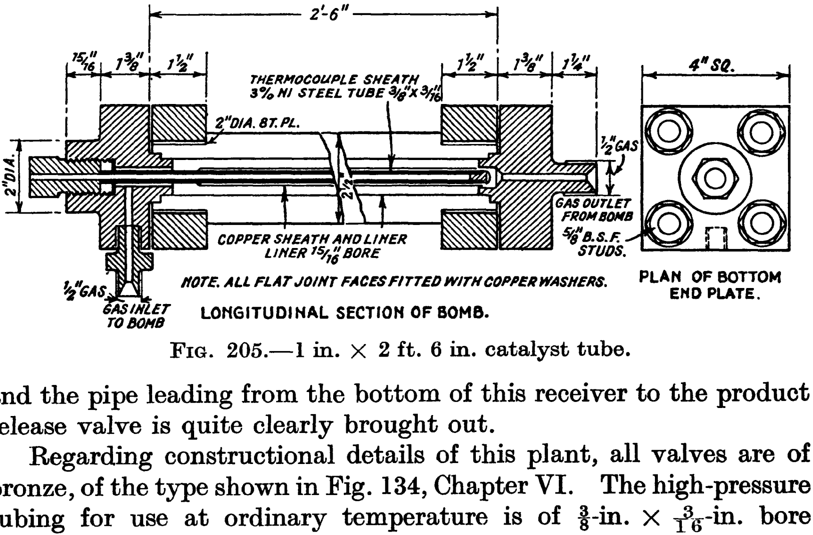

Fig. 205.—1 in. × 2 ft. 6 in. catalyst tube.

Regarding constructional details of this plant, all valves are of bronze, of the type shown in Fig. 134, Chapter VI. The high-pressure tubing for use at ordinary temperature is of $\frac{3}{8}$-in. × $\frac{3}{16}$-in. bore copper, and fittings for this are exactly as Figs. 114, Chapter VI. The preheaters are of $\frac{5}{8}$-in. × $\frac{3}{16}$-in. bore 18 : 8 stainless steel, and these are surrounded by a silica tube 6 ft. long × 2-in. internal diameter, wound with $\frac{1}{2}$-in. wide × $\frac{1}{16}$-in. thick resistance tape. The current supplied for these preheater furnaces and for heating the catalyst tube is at 50 volts.

The catalyst tube is shown in detail in Fig. 205. It is of nickel-chrome-molybdenum steel,* as described for the 2-litre autoclave in Chapter VIII. It is a plain tube 2 ft. 6 ins. long × 1-in. diameter inside and $2\frac{1}{2}$-in. diameter outside. The ends are screwed for flanges 4 ins. square, and the end plates are each secured by four

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* Supplied by English Steel Corporation.

$\frac{3}{8}$-in. B.S.F. studs and nuts, also in the same quality of nickel-chrome-molybdenum steel. The tube is copper lined throughout.

The temperature of the catalyst mass is obtained by a thermocouple free to move up and down a thimble tube within the catalyst tube, as shown. This thimble tube is made from $\frac{3}{8}$-in. × $\frac{3}{16}$-in. solid-drawn steel tube, with one end closed by a screwed plug and brazed. The other end is screwed and brazed to a mild steel pad, which is screwed home against a copper washer as shown. (The thermocouple is of $\frac{5}{32}$-in. O.D. steel tube, with a concentric wire inside of constantan, and insulation is by porcelain beads.) Thus the temperature of any part of the catalyst mass can be obtained. This thermocouple thimble tube is also covered with a copper sheath, and to this copper covering is brazed a copper grid as shown, which serves to support the catalyst.

The catalyst is made by extrusion of a paste of the desired material through an orifice and the resulting vermiform mass is dried and then broken up into little cylinders, about $\frac{3}{16}$-in. diameter × $\frac{1}{4}$-$\frac{3}{8}$ in. long.

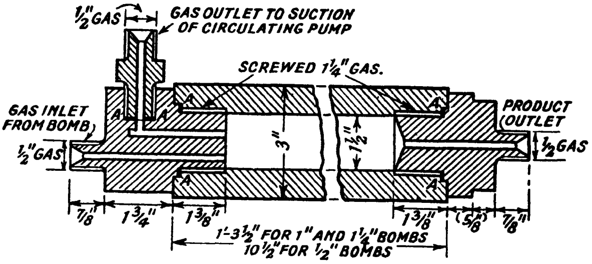

FIG. 206.—High-pressure product receiver, 1 in. × 2 ft. 6 in. circulatory plant.

The gases leaving the catalyst (hydrogen, carbon monoxide and a certain proportion of methanol) are led from the catalyst tube at the top by a $\frac{3}{8}$-in. × $\frac{3}{16}$-in. bore 18 : 8 tube, and pass through a condensing coil made from $\frac{3}{8}$-in. × $\frac{3}{16}$-in. copper tube (about 18 ft. long). The actual coil is about 5-in. diameter, and there are about twelve turns in a length of 1 ft. The methanol is condensed, and falls into the copper-lined mild steel receiver shown in Figs. 206 and 207. Constructional details are given in the sketch. The gases freed from methanol then pass to the suction side of the circulating pump, which is the single-acting Hofer gas-circulating pump described in Chapter II. This pump, when running at 150 r.p.m., has a capacity of 40 litres of compressed gas per hour, and to give an idea of the output of this plant, with a volume of 70 c.c. of basic zinc chromate catalyst, 150 c.c. of methanol are produced per hour at a catalyst temperature of 400° C.

The catalyst tube is heated by means of a winding of ribbon of resistance tape ½ in. × $\frac{1}{16}$ in., wound over a split silica sleeve, ¼ in. thick.

Now, as indicated in Chapter I., the methanol reaction is exothermic, and hence with a plain catalyst tube of the type just described, it is impossible to ensure uniformity of temperature along the length occupied by the catalyst. This difficulty may be overcome by some form of heat interchange device within the catalyst tube.

The other high-pressure circulatory catalyst plant at the Chemical Research Laboratory is fitted with this heat interchange type of catalyst tube. It is in general very similar to that just described, except that the circulating pump is a double-acting Hofer machine of 200 litres per hour maximum capacity, the catalyst tube is as previously stated of the heat interchange type, and there are two condensers and product receivers in series. A photograph of the front view of this plant is shown in Fig. 208, and a rear view is shown in Fig. 209.

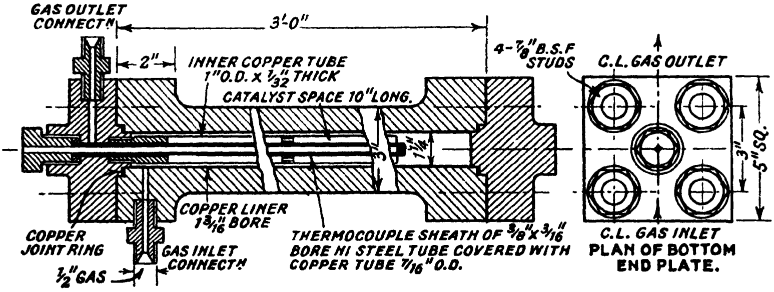
GAS OUTLET CONNECTN
3'-0"
2"
INNER COPPER TUBE 1" O.D. x 1/32" THICK
CATALYST SPACE 10" LONG.
4-7/8" B.S.F STUDS
C.L. GAS OUTLET
3"
1¼"
3"
5" SQ.
COPPER JOINT RING
½" GAS
GAS INLET CONNECTN
COPPER LINER 1 3/16" BORE
THERMOCOUPLE SHEATH OF 3/8" x 3/16" BORE HI STEEL TUBE COVERED WITH COPPER TUBE 7/16" O.D.
C.L. GAS INLET
PLAN OF BOTTOM END PLATE.

FIG. 210.—Section of 1¼ in. × 3 ft. catalyst tube.

A section of the original catalyst tube is shown in Fig. 210. It was of 18 : 8 stainless steel,* and was 1¼-in. internal diameter, 3-in. external diameter, and 3 ft. long. The end flanges were square and the end plates were each secured to the body by means of four ⅞-in. studs and nuts of the same material. The joint was made on a flat copper washer and the joint faces were vee-grooved on the body to facilitate tightness. The interior of the tube was again copper lined. The gas inlet connection was at the side of one of the body flanges. The gas passes up between the inner and the outer copper tubes, thence down through the catalyst mass and out through a side connection tapped into the end plate as shown. The inner copper tube, which contains the catalyst, was secured to the end plate by silver soldering it to a steel nipple, which was screwed home against a copper washer to make a gas-tight joint. The thermocouple thimble tube was constructed in a manner similar to that previously

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* Supplied by Hadfields Ltd.

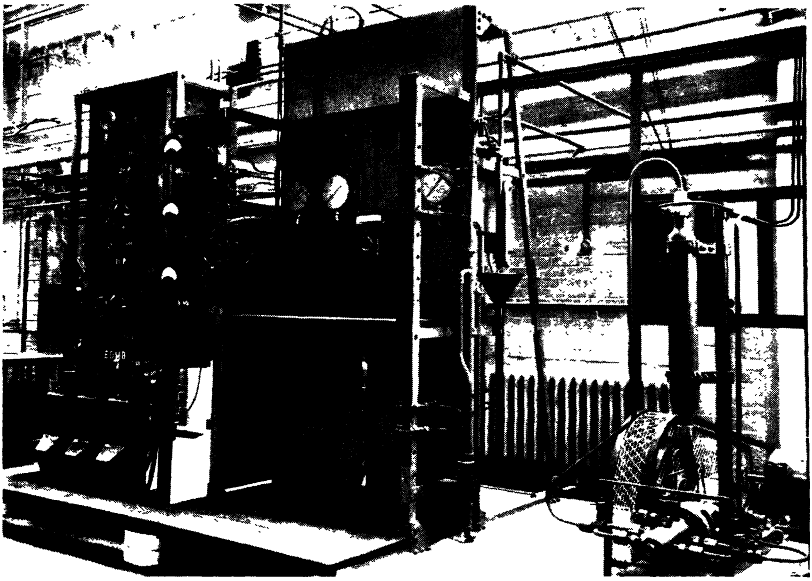


FIG. 208.—Front view of 1¼ ins. × 3 ft. catalyst tube circulatory plant.

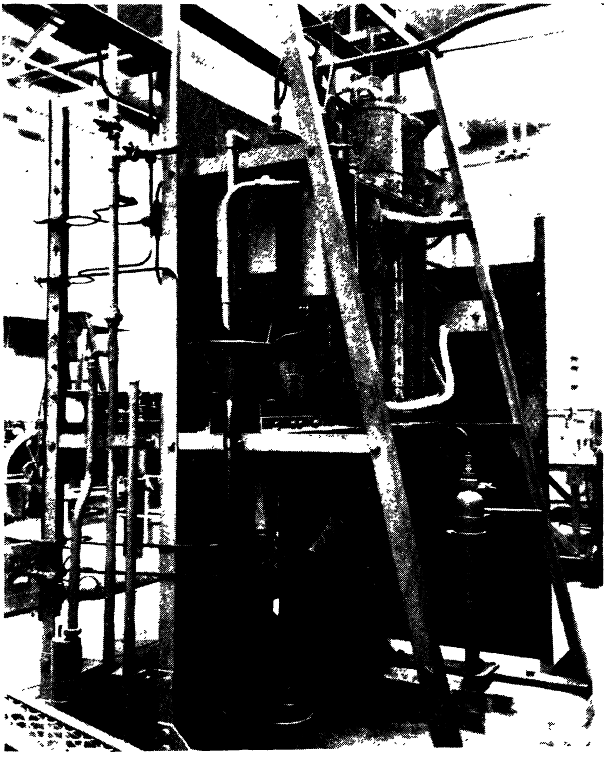


FIG. 209.—Side view of 1¼ ins. × 3 ft. catalyst tube circulatory plant.

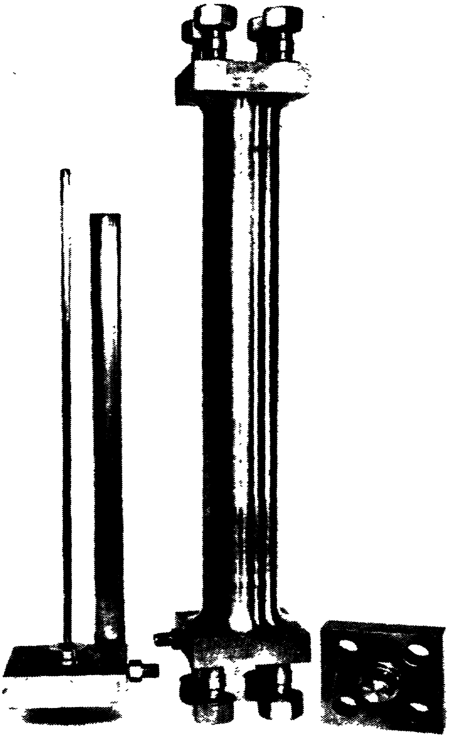


FIG. 212.—Photograph of $1\frac{1}{2}$ ins. × 3 ft. heat interchange type catalyst tube.

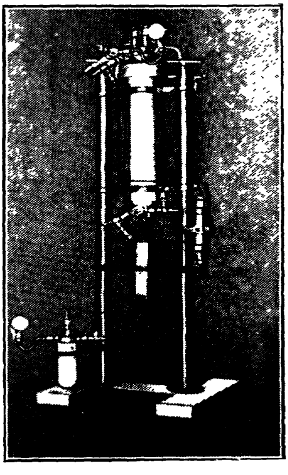


FIG. 215.—Hofer 1000 atm. high temperature circulatory apparatus.

[*See page* 327.

described for the other circulatory plant. In the case of this $1\frac{1}{4}$-in. diameter catalyst tube the catalyst grid was secured to the inner tube, and the thermocouple thimble tube was thus removable at will. The catalyst space was about 70 c.c., and when using zinc chromate catalyst, this plant with the original catalyst tube produced 250 c.c. of methanol per hour.

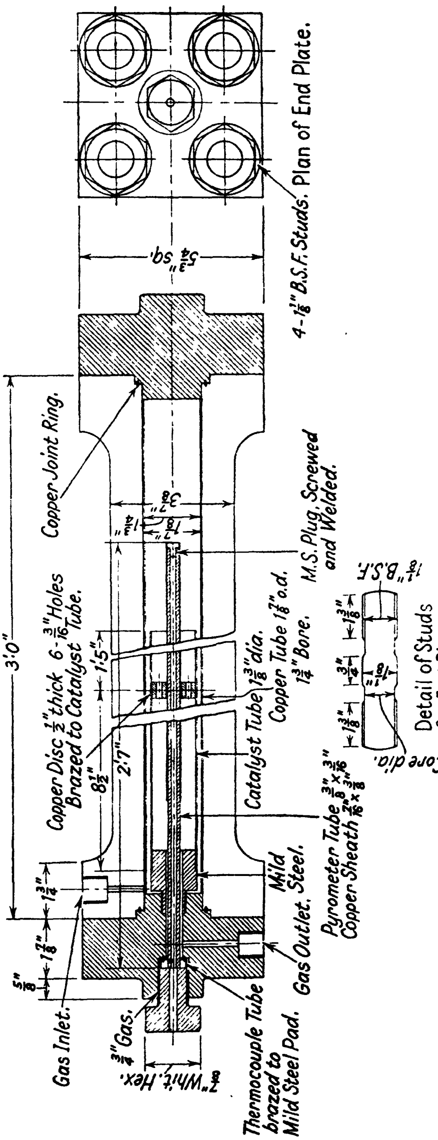

4-1⅛" B.S.F. Studs. Plan of End Plate.
5¼" sq.
Copper Joint Ring.
3⅞"
1¾"
1⅛"
M.S. Plug, Screwed and Welded.
Copper Disc ½" thick 6-3/16" Holes Brazed to Catalyst Tube.
3'0"
1'5"
2'7"
8½"
Catalyst Tube 1⅞" dia.
Copper Tube 1⅛" o.d. 1¼" Bore.
1⅜" B.S.F.
Detail of Studs for End Plates.
Core dia.
Pyrometer Tube 3/8" x 3/16" Copper Sheath 3/16" x 3/32"
Mild Steel.
Gas Outlet.
Thermocouple Tube brazed to Mild Steel Pad.
Gas Inlet.
¾" Gas.
2" Whit. Hex.
1¾"
1⅞"
5/16"

FIG. 211.—$1\frac{1}{4}$ in. × 3 ft. 250 atm. catalyst tube.

The above catalyst tube has recently been replaced by a larger one of nickel-chrome-molybdenum steel. This enlargement gives a catalyst volume of 140 c.c., and the arrangement of this new tube is shown in Figs. 211 and 212.

It will be noted that the catalyst tubes described are externally heated. This, of course, means that the temperature of the walls of the tube must necessarily be a little higher than the gas flowing through, and hence the conditions for corrosion or hydrogen penetration are very favourable. To avoid this in production plants, internal heating is adopted, and the walls of the catalyst tubes are thereby maintained (by suitable internal lagging) at temperatures but little higher than room temperature. In small scale experimental work at temperatures below 475° C. or so, it is often better and cheaper to arrange external heating and scrap the tubes at intervals, thereby avoiding the complications inherent in internal heating arrangements.

Catalyst Tube with Internal Heating.

In instances such as the study of the synthesis of ammonia, where the reaction temperature is 500-600° C., internal heating is, of course, very desirable, even in experimental plants, and Fig. 213 shows a typical catalyst tube as marketed by the American Instrument Co. Ltd., for pressures up to 1000 atms. and catalyst temperature of 500-600° C. The dimensions of the various parts can be gauged from the scale at the foot of the illustration.

The chamber comprises an outer shell of chrome-vanadium steel, bored from solid forged round bar and closed by means of an end plug secured by a cap nut. The joint between the plug and the body is made on a copper washer. A thermocouple tube passes through the end plug and to the interior of the chamber, and terminates in the catalyst mass. The thermocouple tube is closed at the bottom end, and so it resists the full working conditions of the reaction.

The catalyst is heated by internal electric heating, and one of the lead wires for this arrangement is seen passing through the end plug. Insulation is effected by vitreous insulation and a soapstone conical plug (as described in Chapter VI., Fig. 121).

The gas inlet connection is through the end plug, and the outlet is at the side of the shell just beneath this plug. (It will be noted that the catalyst occupies but a very small proportion of the internal volume of the catalyst tube.) The internal arrangement of the chamber provides for a pyrex glass tube $1\frac{3}{4}$-in. outside diameter with walls approximately $\frac{3}{16}$-in. thick and $9\frac{5}{16}$-in. long. Through this is inserted an alundum tube wound with nichrome wire, properly embedded in alundum cement. Finally, a seamless steel tube 1-in. outside diameter × $\frac{3}{32}$-in. wall is inserted through the alundum heating element and this tube forms the actual " test tube " of the chamber. It is customary to place the supported catalytic agent at a point in the steel tube where its centre will be occupied by the bottom of the thermocouple tube. Above and below the catalyst compartment and supported by pieces of copper gauze are packed chips of porcelain or other refractory material.

Referring to Fig. 213, it will be seen that the overall height of the catalyst tube is 15 ins., and the diameter of the vessel is $3\frac{3}{4}$ ins. The approximate weight is 35 lbs., and as arranged in the drawing, it is fitted with connections for use with $\frac{1}{4}$-in. outside diameter × $\frac{1}{16}$-in. inside diameter tube. (Details of standard connections marketed by the American Instrument Co. are given in Chapter VII.)

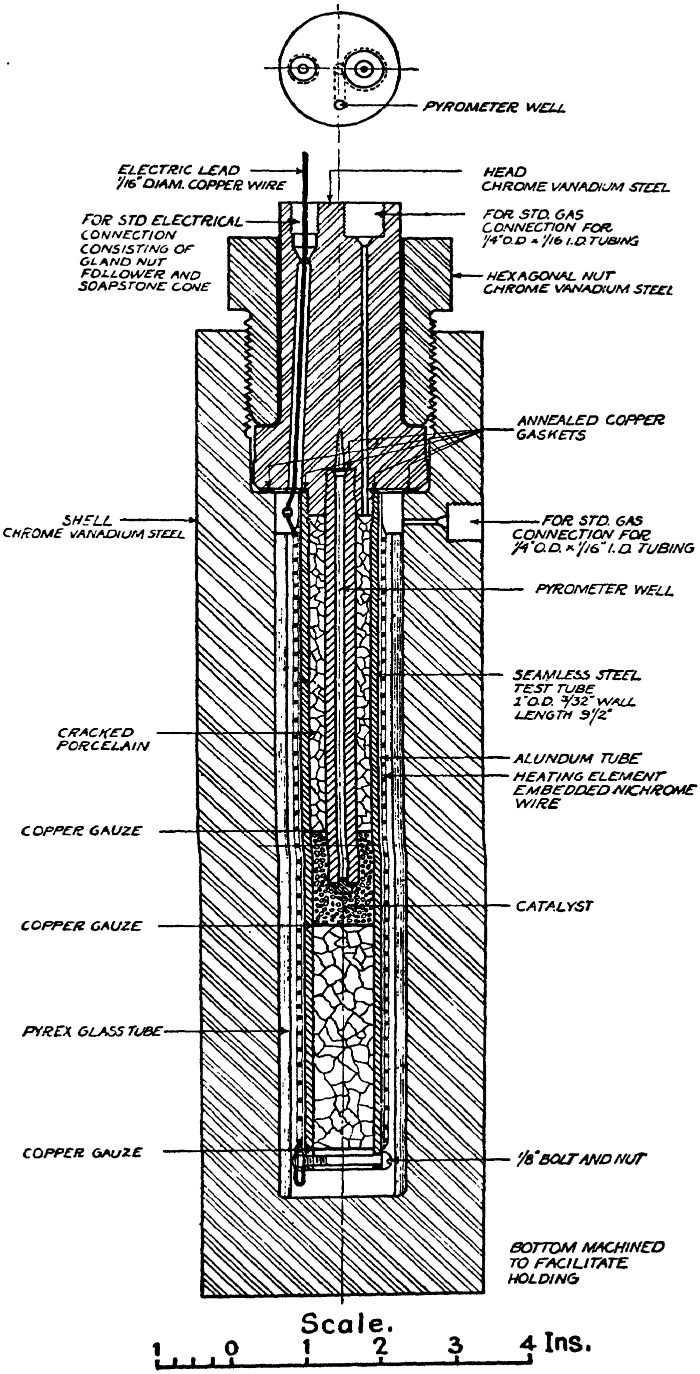

PYROMETER WELL
ELECTRIC LEAD 1/16" DIAM. COPPER WIRE
HEAD CHROME VANADIUM STEEL
FOR STD ELECTRICAL CONNECTION CONSISTING OF GLAND NUT FOLLOWER AND SOAPSTONE CONE
FOR STD. GAS CONNECTION FOR 1/4" O.D × 1/16 I.D TUBING
HEXAGONAL NUT CHROME VANADIUM STEEL
ANNEALED COPPER GASKETS
SHELL CHROME VANADIUM STEEL
FOR STD. GAS CONNECTION FOR 1/4" O.D. × 1/16" I.D. TUBING
PYROMETER WELL
SEAMLESS STEEL TEST TUBE 1" O.D. 3/32" WALL LENGTH 9 1/2"
CRACKED PORCELAIN
ALUNDUM TUBE
HEATING ELEMENT EMBEDDED NICHROME WIRE
COPPER GAUZE
CATALYST
COPPER GAUZE
PYREX GLASS TUBE
COPPER GAUZE
1/8" BOLT AND NUT
BOTTOM MACHINED TO FACILITATE HOLDING
Scale.
1 0 1 2 3 4 Ins.

FIG. 213.—1000 atm. catalyst tube. (American Instrument Co.)

Hofer 1000 *Atm. High-temperature Circulatory Plant.*

An experimental high-pressure catalytic circulatory plant by Hofer for a working pressure of 1000 atms. and a catalyst temperature of 1000° C. is seen in Fig. 214.

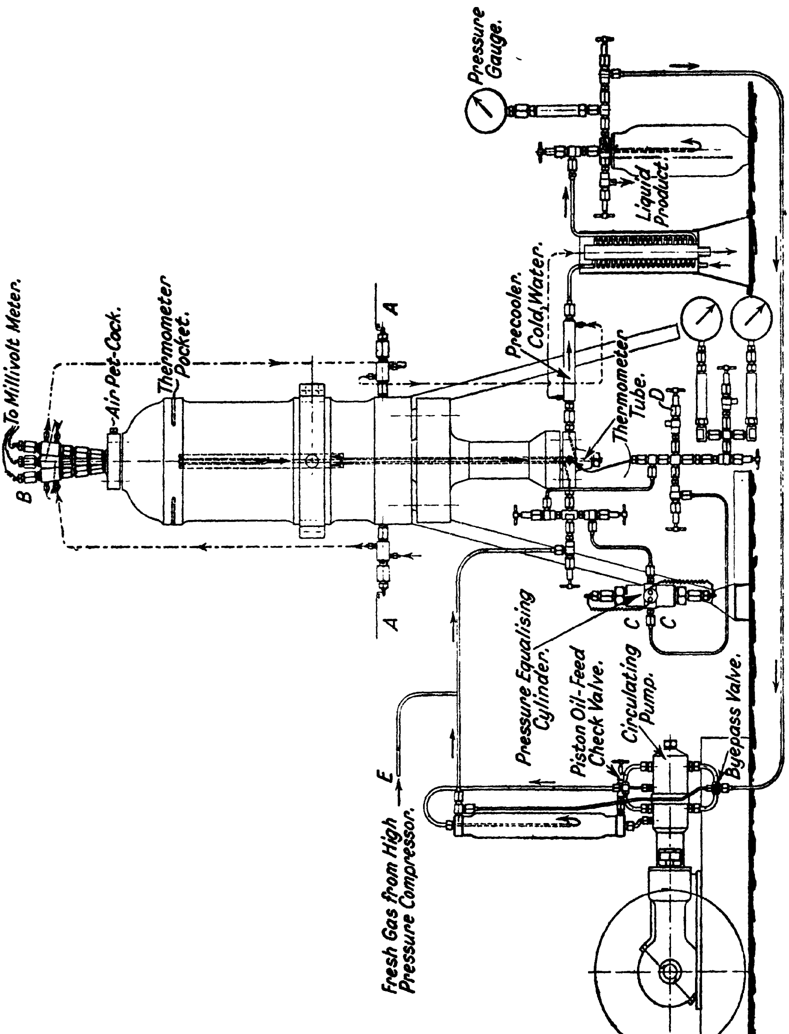


FIG. 214.—Hofer 1000 atm. circulatory plant.

The circulating pump is of the double-acting type, such as was described in Chapter II.

From the circulating pump the contact gases pass to the reaction chamber, which is fitted with internal electric heating, and the terminals (A, A) for this purpose are seen at each side of the lower part of the reaction vessel. Two thermocouples are fitted to record the internal temperature, and the electric connections for these are seen at the top of the reaction vessel (B, B).

A special feature of this apparatus is that the reaction gases do not come into contact with the pressure resisting walls of the reaction vessel. A special protective gas (which may be one of the inert gases) is arranged between the reactants and the vessel walls, and to ensure that the two gases (reactants and buffer gas) are at the same pressure, a pressure equalising device with warning light (C, C) is fitted as shown. The valves here are so arranged that the protective gas need not be used in cases where this protection is not necessary. The inlet for the protective gas is through the valve D.

After passing through the reaction chamber, the gases are led to a cooled tube, and thence through a condensing coil. Any liquid product is condensed and is collected in the receiver provided for that purpose.

The uncombined gases then pass back to the suction side of the circulating pump, and the cycle is repeated. Fresh high-pressure gas is added to the system through a valve on the pipe line E, to maintain the desired reaction pressure. Naturally, the formation and condensation of liquid product causes a continuous drop in the pressure in the system.

Iron-free chrome-nickel alloys are used for the resistance wire for heating the reaction chamber when the catalyst within it is heated to 1000° C. For higher catalyst temperatures molybdenum wire is used. Such reaction chambers are supplied by Hofer with catalyst space up to 500 c.c. capacity.

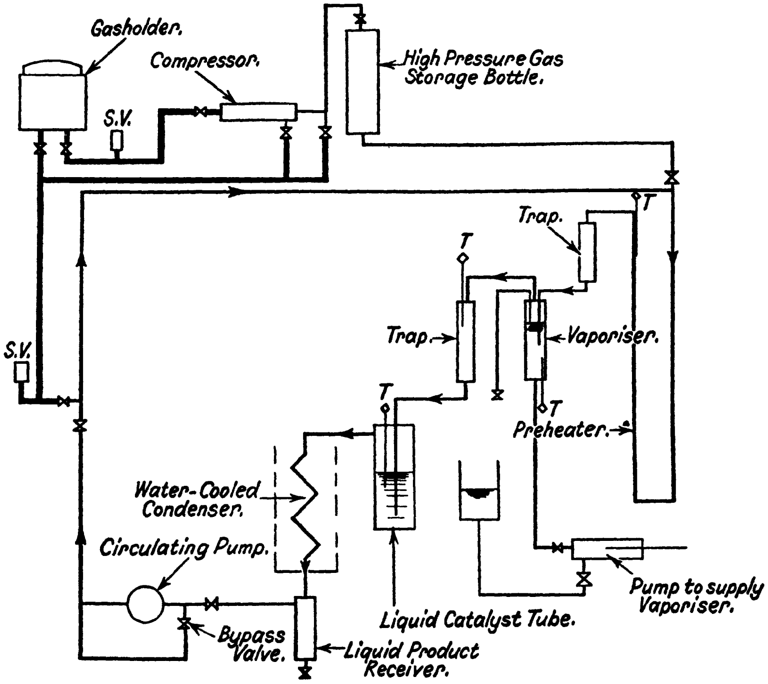
A photograph of the reaction chamber and accessories is seen in Fig. 215.

The reaction chamber is at the top, the condenser immediately beneath it, and the product receiver is seen at the bottom left-hand side. The pressure equalising device (for the reactants and protective gas) with warning light is seen to the right of the tubular support.

High-pressure Catalytic Circulatory Plants with Devices for Introducing Vapour into the Circulatory Gases.

A development of the high-pressure circulatory plants just described is shown in Fig. 216. Briefly it is a circulatory system into which vapour is introduced into the circulatory gases at a definite rate, and in which a liquid catalyst is employed to provide a reaction between the vapour and gases. A typical instance of such processes is that described by the Dreyfus British Celanese, British Patent No. 337,053, in which the vapour of methanol is passed, with carbon monoxide, at a suitable pressure and temperature over a catalyst such as phosphoric acid, and which results in the formation of acetic acid.

Referring to Fig. 216, which gives the layout of a plant of this type designed and built at the Chemical Research Laboratory, the compression system is exactly the same as that described for the synthesis of methanol from carbon monoxide and hydrogen. Assuming that we are dealing with the acetic acid reaction, and that the circulatory plant is running under appropriate pressure-temperature conditions, viz. 150 atms., and a catalyst temperature of 330° C., the gas (carbon monoxide) is first preheated in a preheater of the same type as that previously described for the methanol plants, and thence passes through an empty vessel known as a trap into the vaporiser. This vaporiser is a heated tube 2¼-in. internal diameter and 2 ft. long, and vaporisation is effected by bubbling the incoming gas through the methanol as indicated. The liquid in the vaporiser is maintained at a definite level by judicious manipulation of the supply pump and the overflow valve. (This supply pump is of exactly the same design as the hydraulic test pump described in

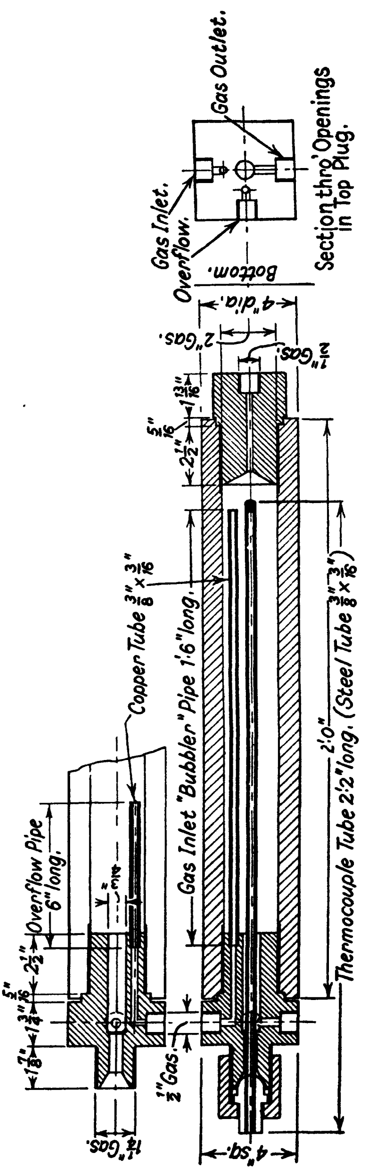


DIAGRAMMATIC LAYOUT OF HIGH PRESSURE CATALYTIC CIRCULATORY PLANT WITH VAPORISER TO INTRODUCE VAPOUR INTO THE CIRCULATORY GASES.

FIG. 216.

Chapter VI., page 182.) The vaporiser is electrically heated and the rate of vaporisation can be readily controlled by varying the temperature of the vaporiser. A thermocouple thimble tube is fitted to the interior of this vessel, as shown in the drawing (Fig. 217). From the vaporiser the mixture of methanol and carbon monoxide passes through a second empty vessel, also known as a trap (which is electrically heated, and the temperature of which is also obtained by a couple inside a thermocouple thimble tube) and thence bubbles through the catalyst contained in a silica tube inside a gas-heated autoclave. Leaving the autoclave, the mixture of carbon monoxide, acetic acid, etc., and unchanged methanol passes through a water-cooled condensing coil, and the condensed liquid is deposited in the receiver provided for that purpose. The gas then passes to the suction side of the circulating pump, and the cycle is repeated.

In plants such as this, where corrosion due to acetic acid is inevitable, special attention must be paid to contact parts. All valves should be made of the appropriate grade of stainless steel, and the same applies to the receiver and the pipework in contact with the liquid mixture containing acetic acid.



Details of Vaporiser. Working Pressure 200 Atm.

Fig. 217.

The two traps are fitted to act as receivers in case of a burst or sudden quick leakage on the delivery side of the circulating pump. In such circumstances the liquid catalyst and methanol in the vaporiser would be driven back through the bubbler tubes, and the traps are provided to prevent damage to other parts of the plant.

When using phosphoric acid as a catalyst in the production of acetic acid from carbon monoxide and methyl alcohol, for brief experiments a silica sleeve for the catalyst vessel is quite satisfactory. The thermocouple tube should also be protected by this material. The inlet bubbler tube is preferably made of silver.

In this connection, the following abstract of a recent paper is of interest (Ryssakov. and Bushmakin, *Zhurmal. Prikladnoi Khimir*, 1932, **5**, 715-721). (Abstracted in *J. Iron and Steel Institute*, February, 1933.)

To determine the most suitable materials for chemical plant used in handling them, the action of phosphoric acid at 105-350° C., under 1-200 atm. pressure, and of molten yellow phosphorus at 80° C., has been investigated on the following metals : steel, copper, lead, and the special alloys V4AE2, V4AE3B, Thermisilid E, Thermisilid (Krupp), Monel Metal, Calite E, Duriron, Hastelloy C, Hastelloy D, silver-copper and silver-nickel alloys at the Russian Institute of Metals. Most of the special acid-resisting alloys are comparatively inert to 65 per cent. phosphoric acid at 105° C., but at 300° C. all the alloys except the two silver ones are severely corroded. Copper is comparatively stable, as the rate of dissolution in phosphoric acid is but slightly affected by rise in temperature. Corrosion is pronounced, however, in phosphorous acid at temperatures above the decomposition point. Silver remains absolutely unaffected by either acid, but is slightly attacked by metaphosphoric acid. Oxygen increases the rate of dissolution of copper, and above 200° C., also of silver in phosphoric acid. Molten phosphorus has no effect on any of the above metals and alloys, except copper and the copper silver alloys, which become covered with a layer of copper phosphide which permeates later into the interior of the metal. At low temperatures the layer is protective against further attack, but at high temperatures the attack becomes rapid.

Hofer supplies a high-pressure catalytic plant with vaporisers suitable for modified reactions of the type just described, i.e. where vapour is introduced into the reaction gas stream. The small model of this type is shown in Fig. 218. It is not provided with circulatory devices, since it is intended as a flow-through apparatus. The design shown is stated to be suitable for 200 atms., at catalyst temperatures not higher than 520° C.

The contact or catalyst tube B is a seamless drawn tube 900 mm. long and 22 mm. internal diameter, within which is a well-fitting liner of copper tube. The closure of this reaction vessel is on the Ipatieff principle, i.e. a disc of soft metal pulled against the two knife-edge facings of the end plate and body by the bolts, as shown.

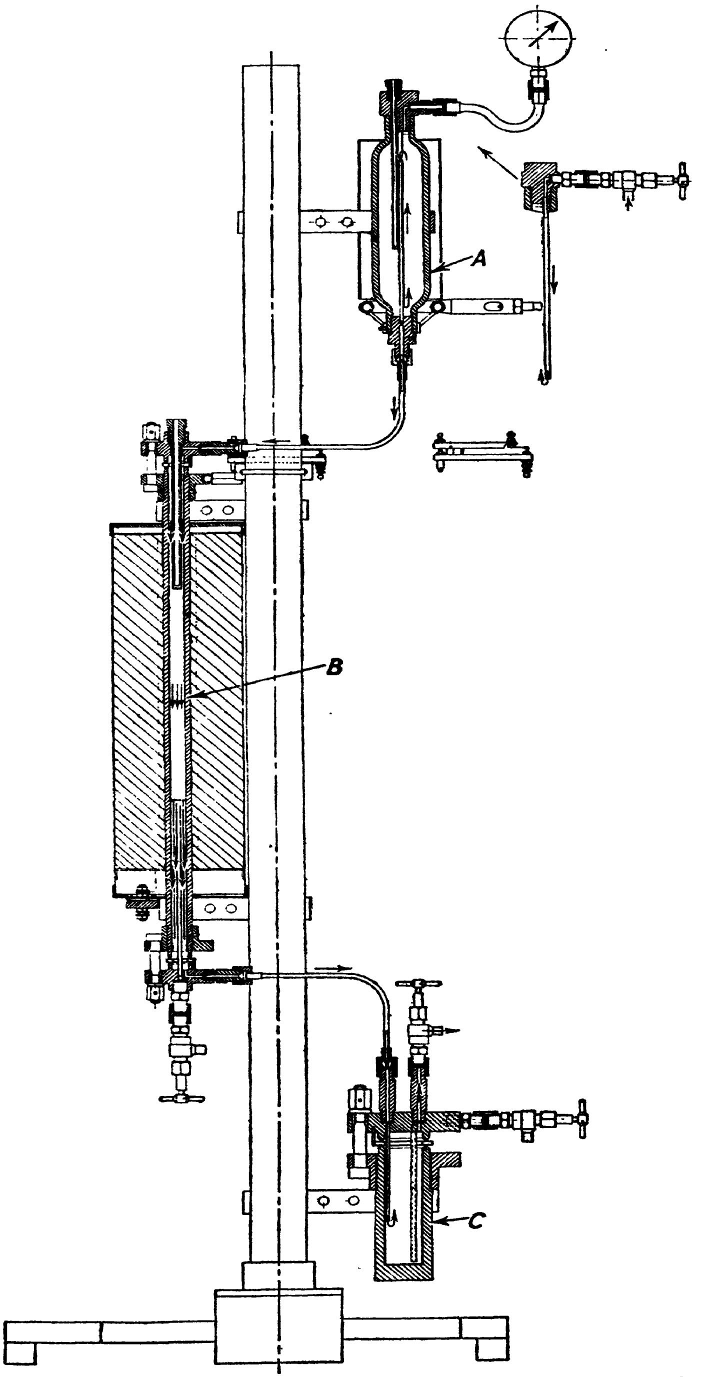


Fig. 218.—Hofer flow-through catalytic plant with vaporiser

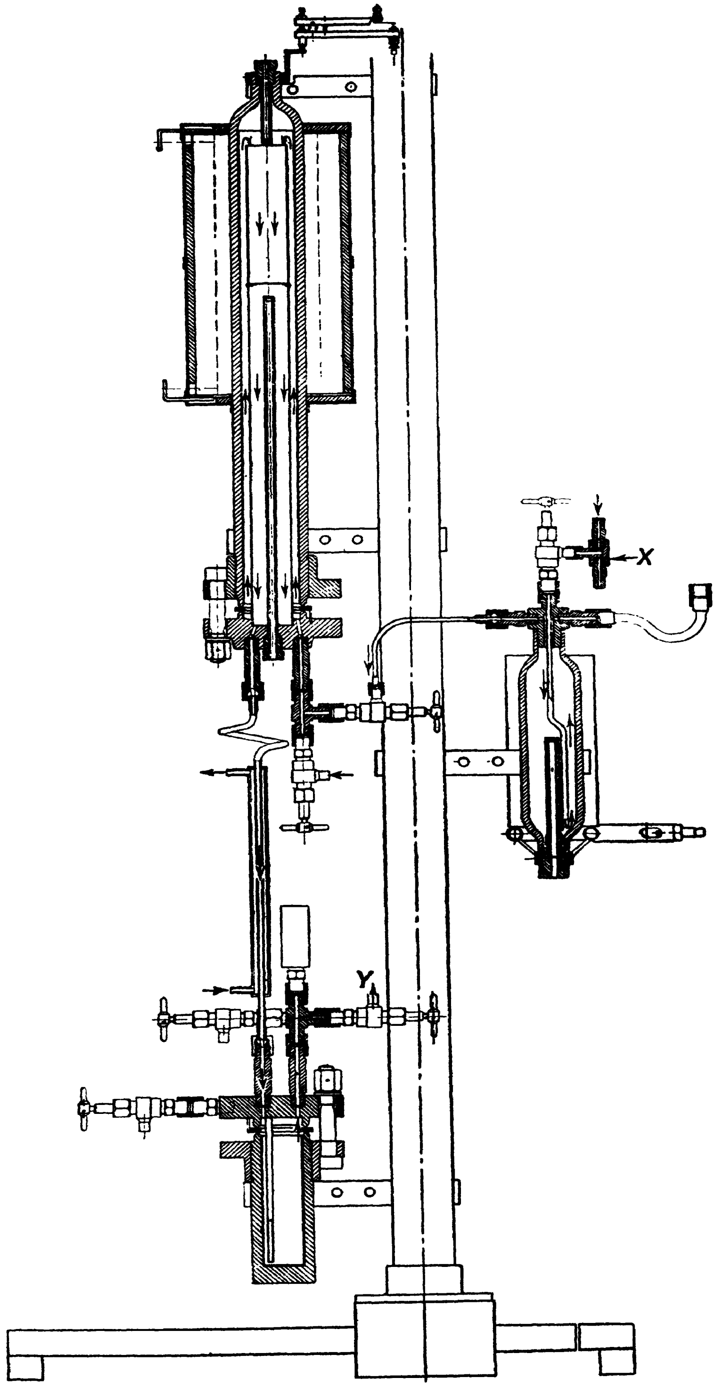


FIG. 219.—Hofer larger circulatory plant with vaporiser.

The temperature of the catalyst space is taken by a thermometer or thermocouple inserted in the thermocouple tube.

The method of operation of the plant is as follows :—

The gas enters the plant by a valve opening in the top plug of vessel A. The gas bubbles through the liquid in the vessel A, and hence is saturated under the particular pressure-temperature conditions obtaining in the vaporiser. The vessel A is gas heated, and a thermocouple tube is provided, as shown, for temperature measurement.

The saturated gas then passes through the reaction tube and thence to the receiver C, where liquid product condenses. The speed of the gas through the plant is so slow that the customary type of water-cooled condenser as used in larger plants is quite unnecessary.

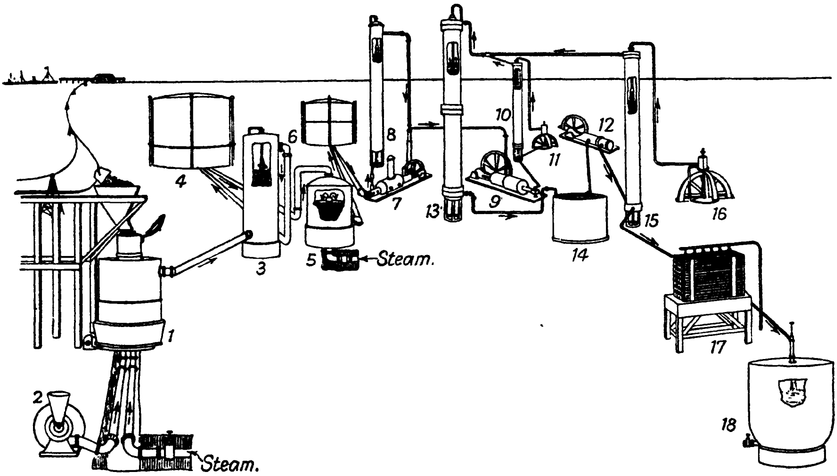


FIG. 220.—Layout of Leuna synthetic ammonia plant: (1) generator for water gas and producer gas; (2) blower; (3) gas purifier; (4) water gas generator and gasometer; (5) catalytic hydrogen plant; (6) contact-gasometer; (7) compressor (25 atm.); (8) plant for removing carbon dioxide; (9) compressor (200 atm.); (10) plant for removing carbon monoxide; (11) wash lye pump; (12) circulation pump; (13) ammonia catalyst chamber; (14) gas cooler; (15) ammonia-absorption tower; (16) high-pressure water pump; (17) water cooler; (18) ammonia liquor reservoir.

The catalyst tube is electrically heated, and a contact arm operated by the expansion of the catalyst tube during heating is so adjusted that at the desired working temperature the current is either reduced or switched off.

A larger apparatus of a similar type by Hofer is seen in Fig. 219. It is suitable for continuous circulation of the gas stream over the catalyst mass, and hence one of the circulating pumps described in Chapter II. is an essential feature of the apparatus.

The gas stream enters the apparatus at X, and after saturation in the vaporiser the mixture passes over the catalyst in the reaction tube, and the liquid is condensed in the straight tube condenser. Separation of the liquid and gas takes place in the receiver, and the gas leaves the plant at Y on its way to the circulating pump for recirculation.

With the exception of the vaporiser, it will be noted that all cover joints of the vessels are made on the Ipatieff principle.

LARGE HIGH-PRESSURE PLANTS FOR THE MANUFACTURE OF AMMONIA, METHYL ALCOHOL, THE HYDROGENATION OF COAL, ETC.

The Haber-Bosch Process.

Regarding commercial plants for the manufacture of synthetic ammonia by high-pressure catalytic processes, brief details of the Haber-Bosch plants were given in Chapter I., and details of the manufacture at Leuna and Oppau of the two reacting gases, hydrogen and nitrogen, were given in Chapter II. Illustrations of the Leuna synthetic plant are shown in Figs. 220, 221 and 222.

The Badische Anilin and later the amalgamated I.G. Farbenindustrie, A.G., have, of course, taken out numerous patents in connection with high-pressure plant, and the following selection of these patents is given to illustrate the trend of development and design in this respect.

B.P. 13,097. *Catalyst chamber for the synthesis of ammonia at high pressure.*

Badische Anilin und Soda Fabrik. May 30th, 1910. (See Fig. 223.)

In the catalytic union of nitrogen and hydrogen to form ammonia, the latter is condensed by abstracting heat from a surface in or forming part of the walls of a vessel in which the combination takes place. A suitable arrangement of apparatus is shown in which the reaction vessel A, capable of withstanding pressure, is surrounded by a cooling-jacket B. The reacting gases enter the apparatus at C, pass up through the catalyst D, which is electrically heated and the condensed ammonia collects at the bottom and is withdrawn through pipe F.

B.P. 208,760. *Apparatus for synthesis of ammonia.*

Badische Anilin und Soda Fabrik. September, 1922. (See Fig. 224.)

The apparatus is provided with an electrical heating device comprising a lead and return conductor of sufficiently large cross-

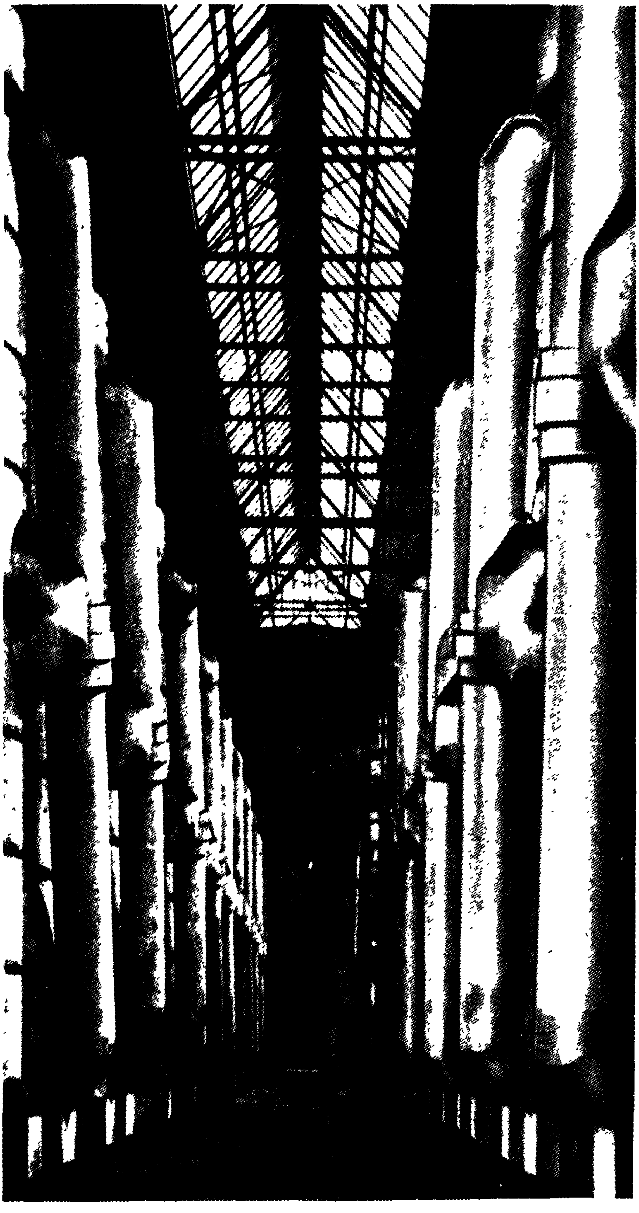


Fig. 221.—I.G. Farbenindustrie, A.G. Catalyst tubes for ammonia synthesis at Leuna.

[*To face page* 334.

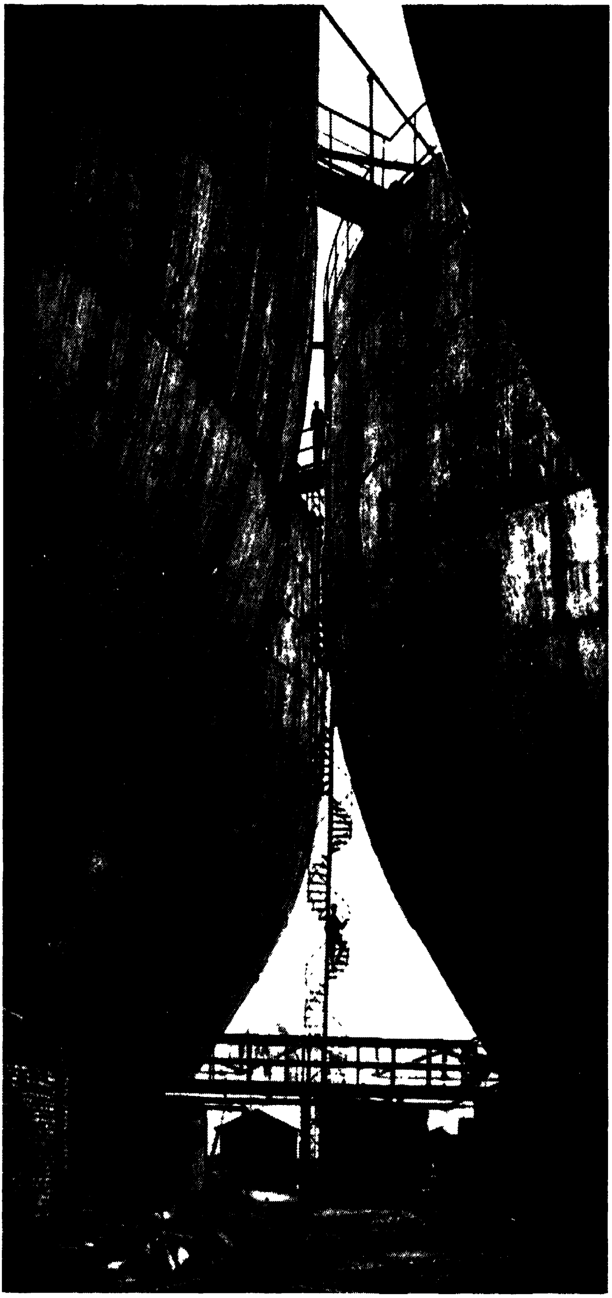


Fig. 222.—I.G. Farbenindustrie, A.G. Ammonia liquor tanks at Leu

[*See page* 334.

sectional area to be self-supporting, the device being adapted for ready introduction into, and withdrawal from, the catalyst tube. In the arrangement shown, the pressure tube (1) for the ammonia synthesis is provided with a tube (3) separating the catalytic material from the heating device, which comprises an outer tube (4) and an inner tube or rod (8) connected at the lower end and having insulators (6) between them. Connections (5) are provided. The reaction gases on entering pass up along the heating device within the tube (3), and then downwards through the catalytic material.

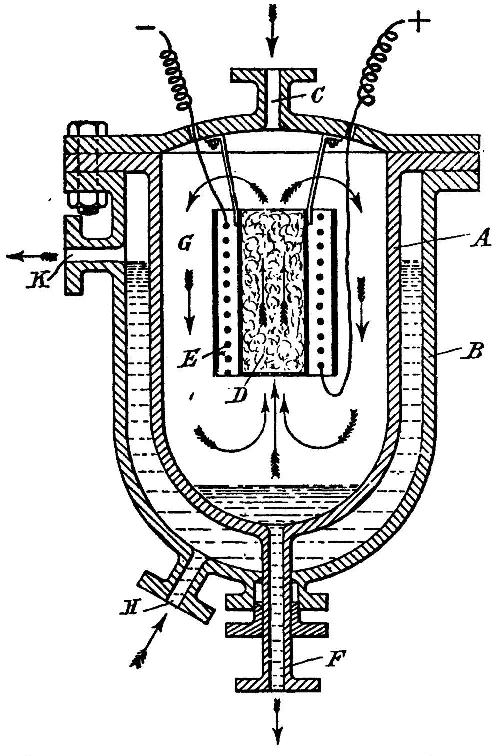


Fig. 223.—Apparatus for the synthesis of ammonia. (B.A.S.F. 1910.)

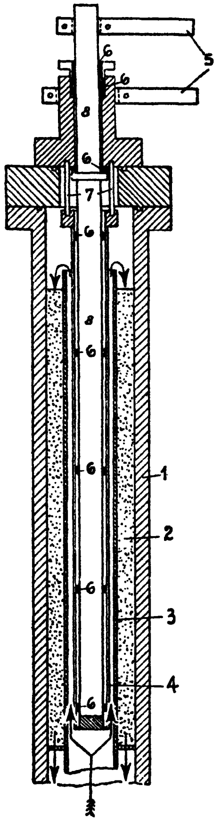


Fig. 224.—Catalyst tube for ammonia synthesis. (B.A.S.F. 1922.)

B.P. 222,461. *Converter or catalyst tube for the synthesis of ammonia.*

Norsk Hydro Elec. Kvall. September, 1924. (This company is a subsidiary of the I.G. Farbenindustrie.) (See Fig. 225.)

The catalyst tube comprises an outer pressure-resisting chamber and an inner catalyst chamber, the walls of the inner chamber being so formed as to allow the passage of the gases through it. To start the reaction the inner chamber may be heated electrically; as shown in the figure, the reaction chamber is formed of a series of rings (9), made of heat-conducting material such as metal or heat-insulating material such as asbestos, the rings being kept in place by bolts (10) fastened to the closure members (4-11) of the outer pressure-resisting chamber.

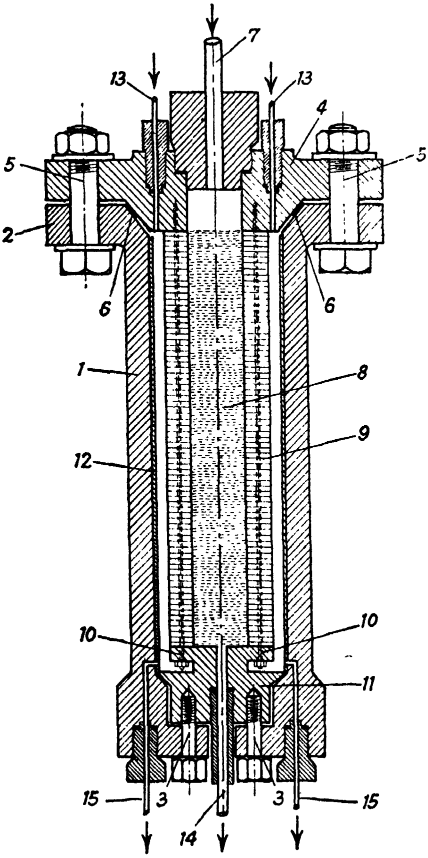


FIG. 225.—Catalyst tube for the synthesis of ammonia. (Norsk Hydro Electric.)

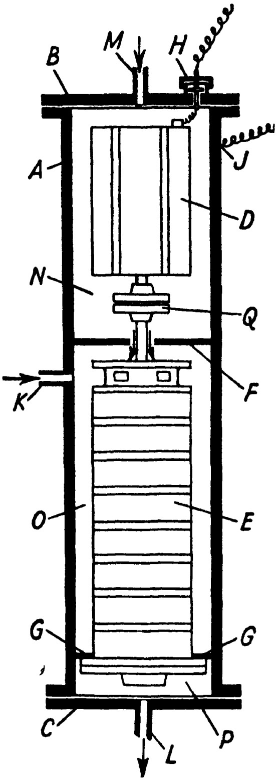


FIG. 226.—Circulating pump for high-pressure gas.

When the synthesis is in progress the gases enter by pipe (7), pass through the catalytic material, escape in part through the rings (9) into the space between the chambers, and issue from the apparatus by pipes (14), (15).

B.P. 245,553. *Circulating pump for high-pressure gas.*

Badische Anilin und Soda Fabrik. November 12th, 1924. (Fig. 226.)

In carrying out reactions between gases and vapours under pressures exceeding 100 atms., the reactants are circulated by means of a multistage centrifugal pump, driven by an electric motor, both of which are disposed within a high-pressure vessel, forming part of the reaction circuit.

Such an apparatus for circulating the gases in the synthesis of ammonia consists of a high-pressure vessel A containing a multistage centrifugal pump E and an electric motor D. The circulating gases enter at K and leave at L, and so as to ensure that no ammonia comes into contact with the motor a partition F is arranged between it and the pump and an inlet M is provided for the introduction of fresh nitrogen and hydrogen.

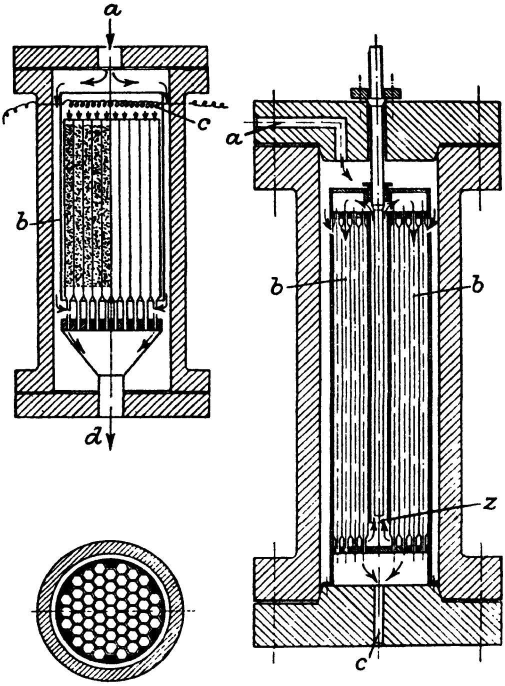


Fig. 227.—Catalyst tube for ammonia synthesis, 1927.
(I.G. Farbenindustrie, A.G.)

B.P. 303,192. *Catalytic apparatus.*

I.G. Farbenindustrie, A.G. September, 1927. (See Fig. 227, i and ii.)

In apparatus for exothermic catalytic gas reactions the catalyst is contained in a number of tubes closely packed together to form a bundle, the interspaces between the tubes being so restricted relatively to the cross-section of the tube, and having regard to the density of packing of the catalyst contained therein, that the incoming gas which passes just on the outside of the tubes travels at a higher velocity than it does within the tubes.

Referring to the Fig. (227, ii) the cold reacting gases enter the catalyst tube at *a*, pass downwards *between* the hot bundle of tubes *b* (which contain the catalyst), and then pass up through the central tube Z, *enter* and *pass through* the catalyst in tubes *b*, and leave the reaction vessel at *c*. In the arrangement shown in i, the cold gases enter at *a*, flow firstly adjacent to the pressure-resisting wall of the catalyst tube; on reaching the end of a guide tube *b*, the incoming gases first pass into the intermediate spaces between the tubes, pass over the electric heating device *c*, and finally enter and pass through the catalyst tube.

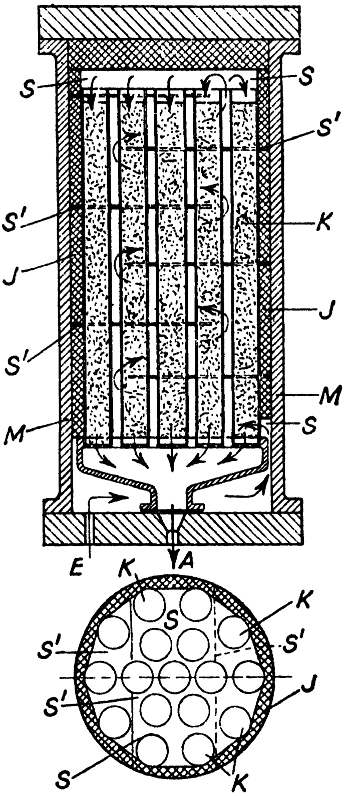


FIG. 228.—Catalyst tube for ammonia synthesis, 1927. (I.G. Farbenindustrie, A.G.)

B.P. 306,054. *Catalytic apparatus.*

I.G. Farbenindustrie, A.G. September, 1927. (See Fig. 228.)

In apparatus for exothermic gas reactions, such as ammonia synthesis, the reaction chamber is cooled by a cooling fluid which flows in a sinuous course around the walls of the reaction chamber. The incoming reaction mixture itself may constitute the cooling agent. The apparatus shown comprises an outer shell M, preferably having a heat-insulating lining J and containing a number of catalyst tubes K. The reaction mixture entering at E flows round the tube K, being diverted into a sinuous course by the baffles S^1, and finally passing downwardly through the tubes.

B.P. 325,557. *Apparatus for the synthesis of ammonia.*

I.G. Farbenindustrie, A.G. September, 1928.

In operating with ammonia, or gases containing ammonia at temperatures above 600° C., the decomposition of the ammonia is lessened by so constructing the apparatus that the gases come into contact only with surfaces of the apparatus consisting of uncombined elementary silicon or substances containing uncombined silicon.

B.P. 317,996. *High-pressure apparatus coated with materials to prevent corrosion.*

I.G. Farbenindustrie, A.G. August, 1928.

In carrying out reaction in the gaseous phase, particularly in the presence of gases such as hydrogen, carbon monoxide or hydrogen sulphide, which attack the material of the apparatus, a small quantity of an inert substance which remains liquid is introduced in such a manner that it forms a protective film on the surfaces of the apparatus. The reaction mixture may be introduced at the upper end of the apparatus, or it may be admitted at the lower end with considerable velocity, so that the liquid is carried up the walls of the apparatus. According to an example, paraffin wax is added to a middle oil which is to be hydrogenated. The application of the process to the synthesis of alcohol is also suggested.

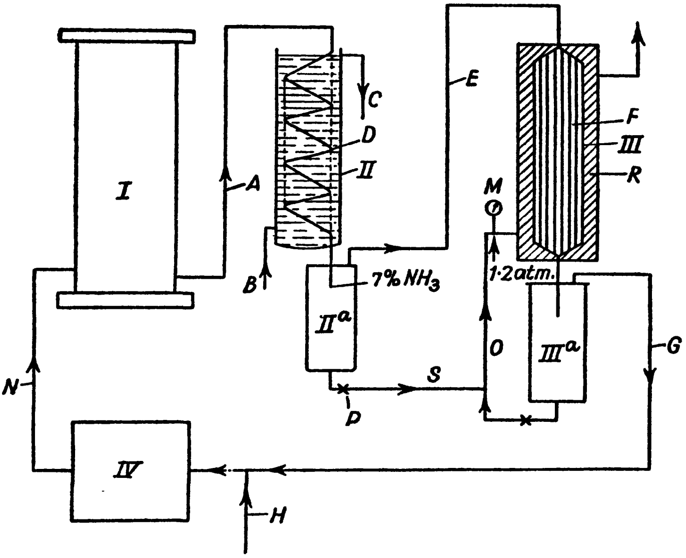


FIG. 229.—Apparatus for the synthesis of ammonia.
(I.G. Farbenindustrie, A.G.)

B.P. 329,079. *Apparatus for synthesis of ammonia.*

I.G. Farbenindustrie, A.G. March, 1929. (See Fig. 229.)

Ammonia is separated from uncombined nitrogen and hydrogen by passage through a cooler in the jacket of which liquid ammonia is evaporated while an inert gas is passed through it. In the illustrated apparatus the gas leaving the reaction vessel (1) passes through a water-cooled condenser (2), and then into a condenser (3). The condensate collecting in the vessels (2*a*), (3*a*), together with a portion of the uncombined gases, is withdrawn, and passed through the jacket R of the condenser (3) at a pressure of 1-2 atms. The remainder of the uncombined gas is recirculated to the reaction vessel.

The Claude Synthetic Ammonia Process.

The Claude process is remarkable for the high pressure employed, viz. 1000 atms. M. Claude has published quite a lot of information (most of which appears in *Comptes Rendus*) about his reasons for the choice of such a high pressure, and his subsequent early difficulties with the plant. The use of this high pressure has certain very definite advantages. Firstly, the equilibrium mixture at 1000 atms. and 550° C. contains about 40 per cent. of ammonia, as against 13 per cent. at the lower pressure used in the Haber-Bosch process. These high conversion rates are very economical as regards power. An increase of pressure from 100-1000 atms. necessitates only half the power required to compress the same mass of gas from 1-100 atms. Another important advantage of working at 1000 atms. is that the ammonia produced is available in liquid form from the receivers of the plant. Those plants working at a lower pressure have to provide special means for absorbing the ammonia, either in cold water or other fluid, or by external refrigeration.

Compressors and circulating pumps suitable for 1000 atms. working pressure were described in Chapter II., and in the subsequent chapter details were given of the Claude process for the production of hydrogen from coke-oven gas.

A description of a 25-ton unit Claude synthetic ammonia plant (i.e. an output of 25 tons of ammonia per day) is as follows. (See Fig. 230.)

The hydrogen and nitrogen drawn by the compressor from their respective gasholders are united and mixed in suitable proportions by automatic apparatus. The gas is compressed to 1000 atms., and thence passes to the synthesis tubes, of which there are five.

The first catalyst tube is called a purifying tube, and it eliminates the last traces of impurities (carbon monoxide where the hydrogen is produced by the liquefaction-separation of coke-oven gas or oxygen in the case of electrolytic hydrogen); this purification is accomplished by a catalytic reaction, in which carbon monoxide is converted to methane and water, and oxygen to water. The gas leaving this purifier tube is cooled, passed through a separator, where the water formed is deposited, and is then conveyed to the first producer catalyst tube.

In this first producer tube the nitrogen and hydrogen combine and yield ammonia until equilibrium is reached. The mixture of hydrogen-nitrogen-ammonia is cooled on leaving the tube, the anhydrous ammonia is condensed, and falls into a separator, where it is drawn off. The gas, free from ammonia, then passes to the

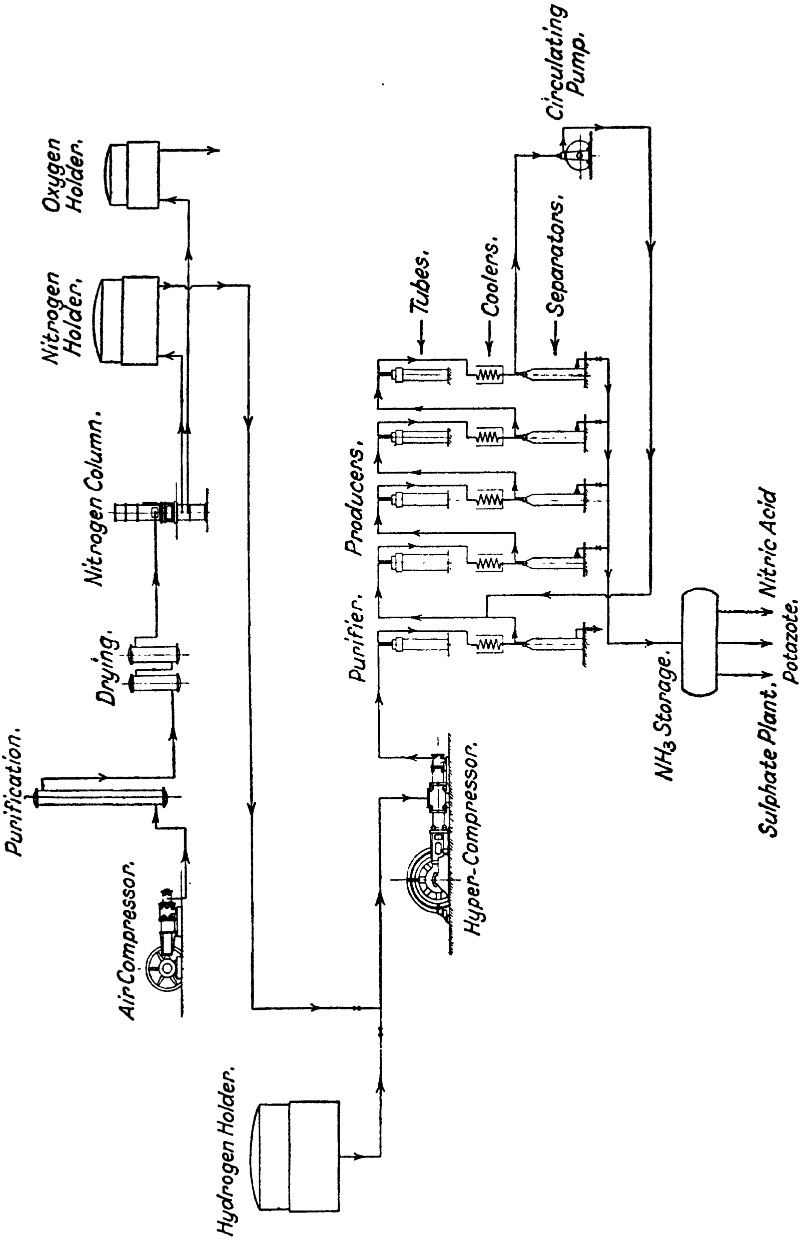


FIG. 230.—Layout of Claude synthetic ammonia plant.

second tube, where more ammonia is produced; ammonia is once more removed by cooling, and the third and fourth catalyst tubes function in the same manner.

On leaving the last tube the gas (which is but a small fraction of the original gas volume) is taken up by a circulating pump which raises the pressure to 1000 atms. before recirculation with additional gas supplied by the compressor.

The catalyst tubes of the 25-ton units are of ordinary steel. They contain the catalyst, the electric heating arrangements, and the insulating jackets. The wall of ordinary steel, which is stressed by the internal gas pressure, is efficiently protected from the effect of the high reaction temperature by insulation, and various patented devices, so that the temperature of this stressed tube wall never exceeds 160° F. Under these conditions, the metal is quite unattacked by hydrogen or ammonia. The electrical heating device serves to initiate the reaction, the temperature of which is subsequently maintained by the reaction heat.

The catalyst is enclosed in a special envelope or cartridge attached to the closure cap ; a closure system controlled by hydraulic jacks assures gas tightness and permits of the replacement of the used catalyst cartridge in less than one hour.

Units of capacity smaller than that described are constructed on very similar lines ; units of less than 10 tons daily capacity are preferably fitted with catalyst tubes of a special alloy known as BTG (made by the Societe de Commentry-Fourchambault et Decazeville of Imphy, France) which resists pressures of 1000 atms. at a temperature of 1000° F. This method very much simplifies the protective and heating apparatus. The alloy BTG was described in Chapter VII., and tubes made of this material have been found to have a long useful life.

Photographs of plants using the Claude process are seen in Figs. 231, 232 and 233.

It will, of course, be realised that many difficulties had to be overcome before the Claude process became the commercial success which it is to-day. Quite apart from compression difficulties, perhaps Claude's biggest problem was the removal of the heat generated by the reaction. With conversion rates five or six times as great as that of the Haber-Bosch process, this problem was not easy of solution, as will be seen from the following selection of the British patents taken out by L'Air Liquide* during the past fifteen years or so.

B.P. 140,083. *Improvements relating to protection of the walls of reaction vessels at high temperatures and pressures.*

L'Air Liquide, 1920. (See Fig. 234).

This invention relates to enclosures of the kind in which reactions take place at a high pressure and temperature and in which protect-

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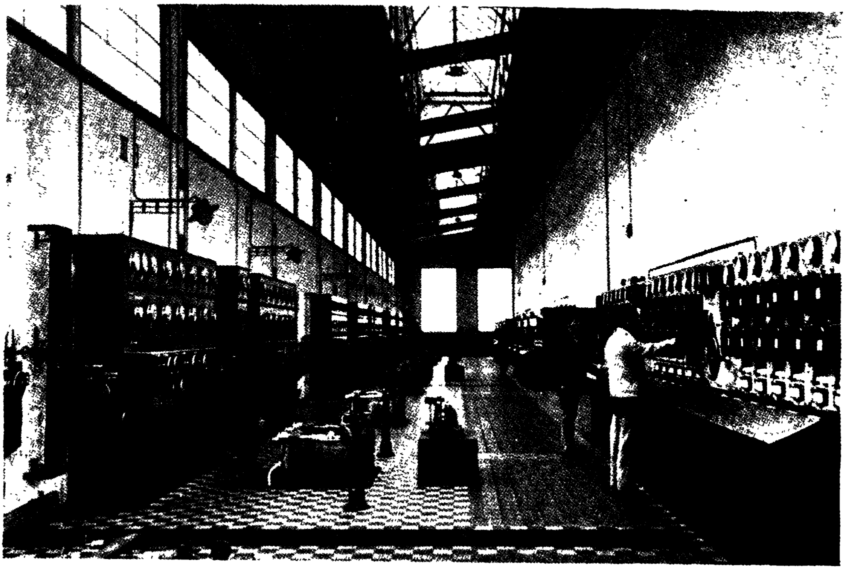
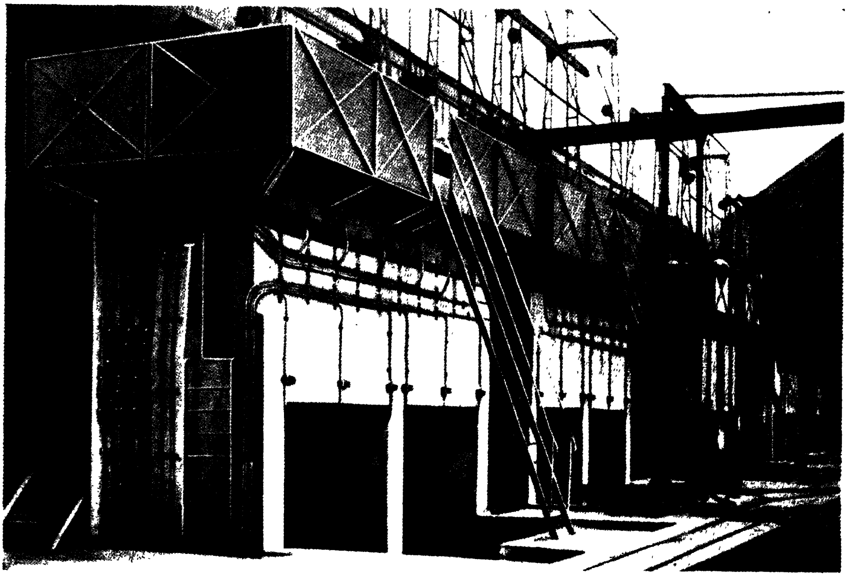
* *This Organisation is responsible for the development of the various Claude processes.*



Control board for Claude synthetic ammonia plant. (Rauxel factory.)



Five 7·5-ton catalyst tube units, Claude synthetic ammonia plant. (Waziers factory.)

FIG. 231.

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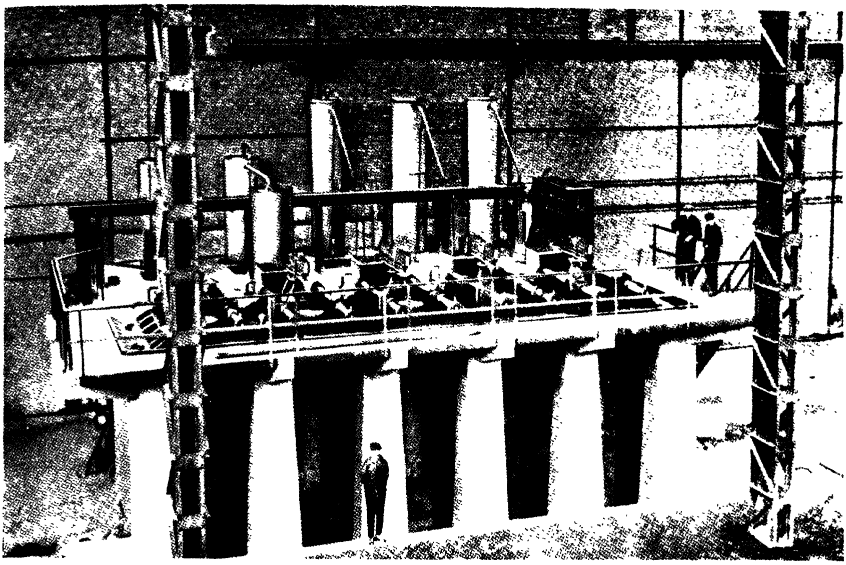
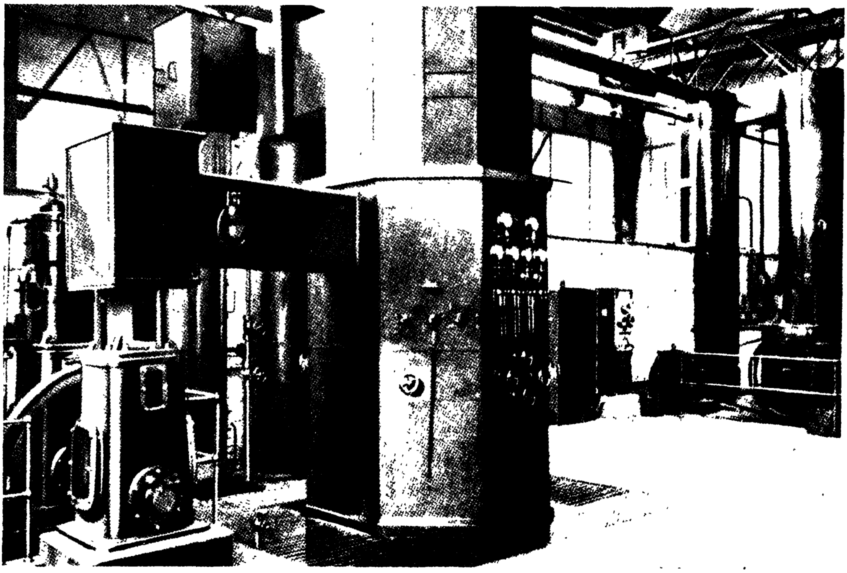


25-ton catalyst tube unit, Claude synthetic ammonia plant.
(Ougrée factory.)



Nitrogen column, Claude synthetic ammonia plant. (Waziers factory.)

FIG. 232.

[*See page* 342.

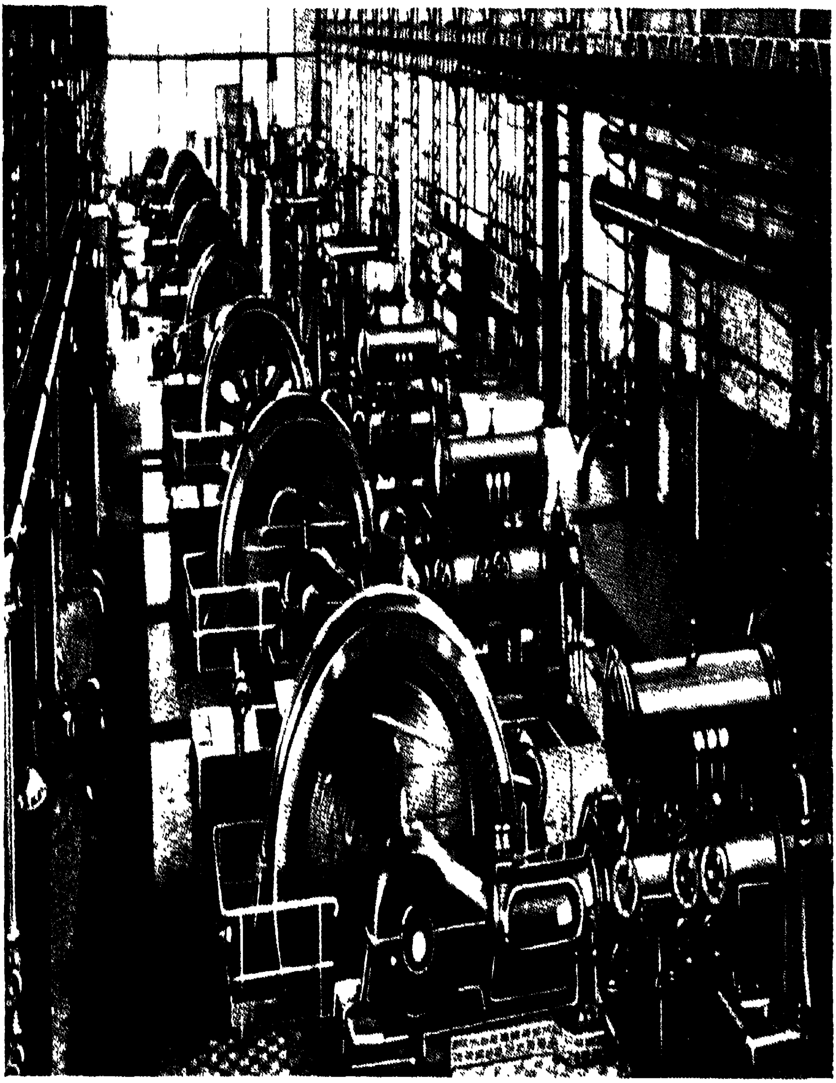


FIG. 233.—Compressor room, Claude synthetic ammonia plant, Bethune.

[*See page* 342.

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ing means are employed which consist in providing, in contact with the pressure-resisting walls, a layer of a liquid which is stable and not very volatile at the temperatures prevailing within the vessel during the reaction. The liquid is preferably one which is a bad conductor of heat, and which is rendered stationary by means of solid material which is very little or not at all attacked by it and which is also a bad conductor of heat. In the event of one of the reacting substances being hydrogen, as for example in the synthesis of ammonia, the said solid body or the liquid itself may be of such a nature that the hydrogen (that may enter the liquid by dissolving therein and by this means reach the wall to be protected) is absorbed.

The present application relates to an improvement on this invention and consists in the use of solid material in the form of a tube, or of superposed rings which offer a more effective resistance to the movements of the liquid and of the hydrogen than a mere filling of fragments.

The figure shows a section of one form of the apparatus and a section of part of a modified form.

Referring to the accompanying drawings, T is the tubular enclosure to be protected, the cold end being at the bottom. The tube may be arranged with its axis inclined or vertical as shown. T_1 is the metal tube intended for the purpose of confining the half-solid, half-liquid chemically and thermally protective wall. J is the conical joint for the purpose of preventing the liquid from escaping.

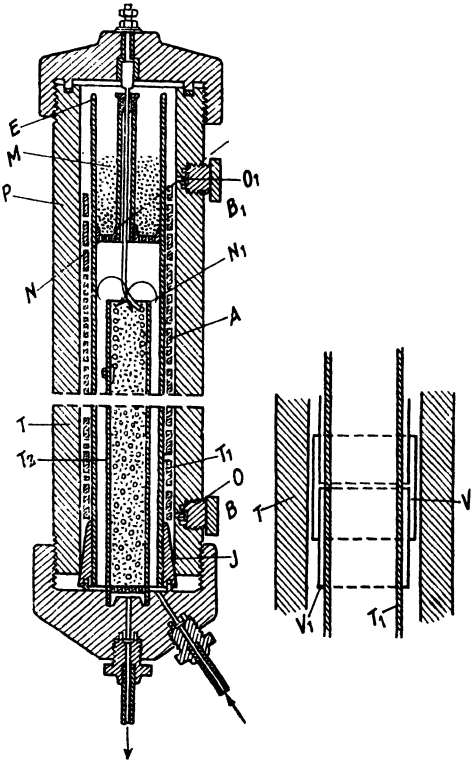


FIG. 234.—Catalyst tube. (L'Air Liquide.)

The tube T_1 is continued to the other end of the apparatus, but its extremity E at this end is free to provide the clearance necessary to permit of expansion. The catalysis chamber terminates at N_1 below the level N that is to be reached by the liquid. In the annular space between T and T_1, a pile of rings of the selected material, magnetic oxide of iron for instance, is first arranged, and then, the apparatus being closed and heated to the desired temperature, the selected liquid, a potash-soda mixture for instance, is forced up through the aperture at O, under the action of a slight pressure and heated to the appropriate temperature, until the liquid overflows through the aperture O_1 provided at the desired level, which, as well as the aperture O, are then closed, by means of screwed plugs, B, B_1. Owing to the fact that the tubular catalysis chamber T_2 reaches a level N_1 lower than the level N of the liquid and that the circulation path of the reacting gases also does not pass beyond N_1 the temperature of reaction is localised a long way from the end of the tube, and the liquid bath, limited to the level N, where a comparatively low temperature prevails, only leaves uncovered portions P of the tube T which are not hot enough to be attacked by hydrogen or ammonia. This method of carrying out the invention is advantageous in that the incoming gases rise between T_1 and T_2, while they are being heated.

As evidence in favour of the use of the potash-soda mixture and of the iron oxide screen, it has been ascertained that the first, even under pressures of 1000 atmospheres, only dissolves insignificant quantities of hydrogen, less than one-fifth of its volume reckoned at atmospheric pressure, and that on the other hand fused magnetic oxide of iron, such as is obtained when cutting iron by means of oxy-flames, and notwithstanding its great compactness and its great hardness, is reduced to iron by hydrogen at the pressures employed, and at temperatures below 500° C.

The quantity of water vapour produced is small, and insofar as it is not removed by the potash-soda mixture, it may be removed by causing it to pass through an absorbent substance, reduced iron for example, before being diluted by the reacting gaseous mixture. The iron is for this purpose placed at M, in a region where the temperature is still sufficient to effect the reduction of the water vapour.

A modification of the device, consisting of rings arranged one over the other, is also illustrated. The protecting screen may consist of two or more concentric layers of rings V_1, V_2 of material which is a bad conductor of heat, arranged so as to stagger the joints of the layers with respect to one another, in order to obviate any possibility of radial motion of the liquid which surrounds the rings between the two tubes T_1 and T.

The invention states that cracks or fractures that may be produced in the rings do not in practice impair the effectiveness of the screen they form, the cross-sectional area of the streams of liquid through these fractures or cracks in radial directions being negligible in comparison with the total cross-sectional area which would exist for the passage of the liquid if there were no screen.

B.P. 161,195. *Apparatus for synthesis of ammonia.*

L'Air Liquide. April, 1920.

In the synthesis of ammonia under conditions of high pressure, the development of stresses in the wall of the pressure tube due to the difference in temperature between the inside and outside layers of the wall is minimised by heat insulating the exterior wall, thereby maintaining a fairly uniform temperature throughout the thickness of the metal.

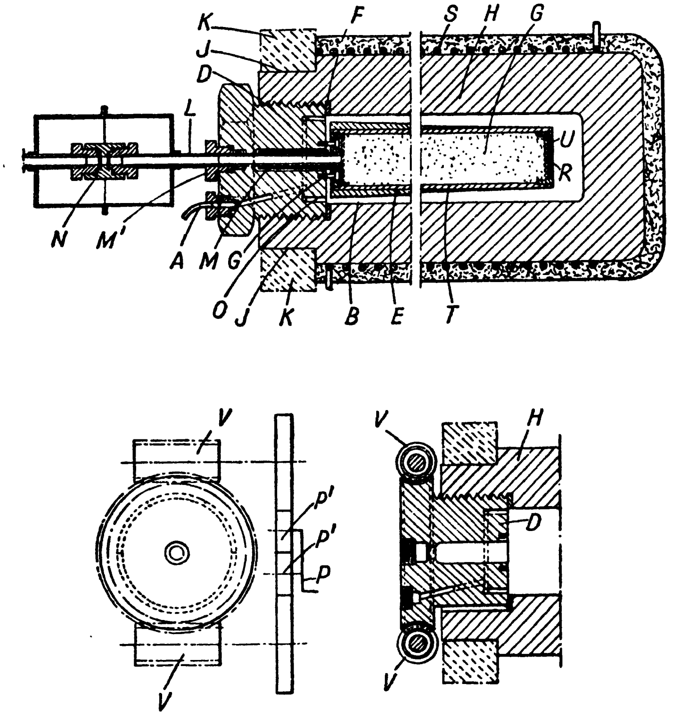


FIG. 235.—Catalyst tube for ammonia synthesis. (L'Air Liquide.)

B.P. 174,041. *Apparatus for synthesis of ammonia.*

L'Air Liquide. January, 1921. (See Fig. 235.)

To facilitate the renewal of the catalytic material, the inner tube containing the catalyst is rigidly secured to the removable head of the permanently fixed outer pressure tube. The inner tube T containing the catalytic material is mounted on the exit tube L which passes centrally through the screwed head D of the pressure tube H. By unscrewing the head D the inner tube T is withdrawn, and can be refilled after removal of the gauze plug R. The screw thread or the head D may be continuous, but is preferably interrupted like that of a breech gun block. The pressure tube H is made of a metal adapted to resist the action of the gases present, such as the alloys ATG and BTG, the composition of which is described in B.P. 140,508 and 159,857. (See also Chap. VIII.)

B.P. 268,721. *Apparatus for the synthesis of ammonia.*

Soc. L'Air Liquide. March, 1926.

In the synthesis of ammonia and other high-pressure catalytic processes, and with absorption of the heat of reaction by the fresh reaction gases, there is circulated between the container for the catalyst and the outer pressure-resisting wall a gas which maintains the temperature of the wall within safe limit, and is discharged outside the pressure tube. After cooling the gas may be used again for the same purpose.

B.P. 268,722. *Catalytic apparatus.*

Soc. L'Air Liquide. April, 1926.

In exothermic reactions such as the synthesis of ammonia heat is conveyed from hotter to cooler parts of the catalytic mass by means of the reaction gases before they come into direct contact with the catalyst. This is done by an arrangement of gas tubes inside the chamber.

B.P. 275,592. *Catalytic apparatus.*

Soc. L'Air Liquide. August, 1926. (See Fig. 236.)

In apparatus for carrying out exothermic reactions the gases, after leaving the catalyst, are passed without further heat transference into indirect contact with the hottest zone of the catalyst, and then circulated in indirect contact with the cooler zones of the catalyst. As shown in Fig. 236 (1), the reagents enter the reaction chamber by an annular passage A and pass through tubes B into contact with the catalyst; the reagents may be preheated or heated by electrical means within the chamber. The gases traverse the catalyst mass and the reaction products pass at D into a tube E which conveys them to the hotter end of the chamber, whereafter they leave the chamber by the annular passage X and the tube Y. Several tubes E, X, may be provided, and the chamber may be externally cooled. Other modifications of this principle are given.

B.P. 288,577. *Improvements relating to processes for carrying out catalytic chemical reactions.* (See Fig. 237.)

L'Air Liquide, 1928.

This invention relates to processes for carrying out exothermic catalytic chemical reactions under pressure, and has particular reference to the synthesis of ammonia from its constituent elements. The present process is applicable in circumstances when the reaction is carried out on a mixture of fresh gases and gases containing ammonia, for example when the gaseous mixture circulates several times over the same catalysing material located in one or several apparatuses in series, and is supplemented by fresh gases before each passage over the catalyst.

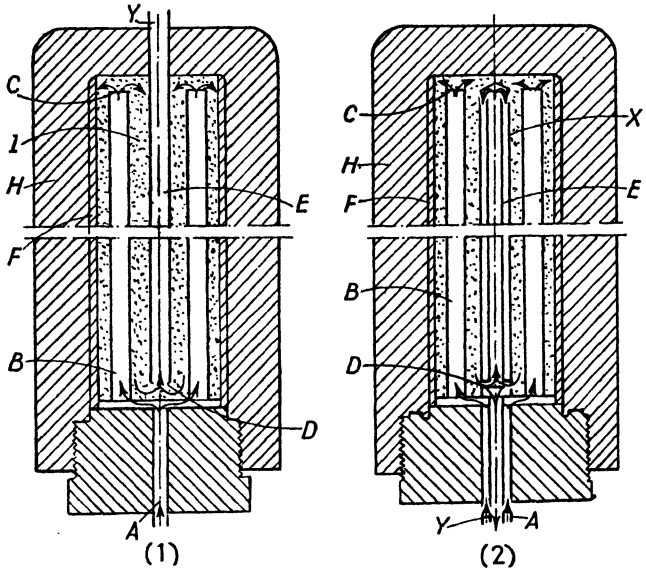


Fig. 236.—Catalyst tube for ammonia synthesis. (L'Air Liquide, 1926.)

The principal object of the invention is to prevent the above-mentioned gaseous mixture containing ammonia coming into contact with and thereby weakening the pressure-supporting walls of the reaction apparatus. With this object in view, according to the present invention, the fresh gases are fed into the space between the pressure-supporting wall and an interior tube containing the catalysing material so as to protect the wall from the temperature produced by the reaction. The fresh gases are then mixed, after they have been thus heated, with the gases containing the products of reaction, and the mixture so obtained is then passed over the catalysing material.

The catalysing apparatus, Fig. 237, comprises an outer pressure-supporting container A and an inner receptacle B containing the catalysing material Y, the walls of the containers A and B being separated by an annular space E between them. Inside the container there is also located a heat exchanger C which permits heating of the gases immediately before the reaction at the expense of the heat contained in the hot gases leaving the catalysing substance.

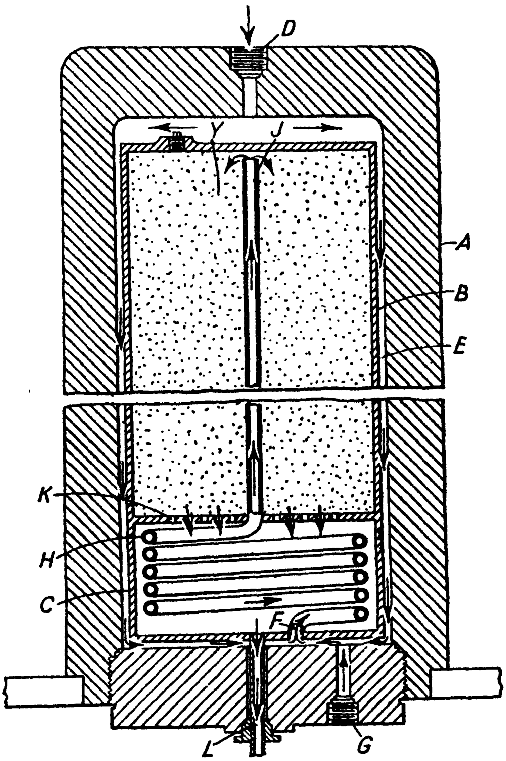


FIG. 237.—Catalyst tube for ammonia synthesis. (L'Air Liquide.)

The compressed fresh gases, composed, for instance, of a mixture of nitrogen and hydrogen for the manufacture of ammonia, enter the apparatus through the inlet D, and pass through the annular passage E, where they protect the wall of the outer receptacle A from the heat produced by the reaction, and at the same time remove a certain amount of this heat through the wall of the catalyst receptacle B. The gases thus partially heated enter the heat exchanger C through the orifice F, along with the ammonia-containing gases which enter the apparatus through the inlet G. The mixture of the fresh and ammonia-containing gases then passes into the coil H of the heat exchanger C, where it is heated by the out-going gases passing over the coil H. The gaseous mixture thus heated then passes through the pipe J, where it is further heated by heat exchange with the catalysing material and the reacting gases in contact therewith. On arrival at the end of the pipe J the gaseous mixture flows in the reverse direction, but in direct contact with the catalyst, where it reacts to form ammonia. The gaseous products of the reaction leave the catalyser through the orifices K, pass over the coil H, and leave the apparatus through the outlet L. The gaseous products are then treated for the removal of the ammonia, for instance by cooling them in a liquefier, and the uncombined mixture of nitrogen and hydrogen, together with the uncondensed ammonia, is then returned by a circulating pump (not shown), so as to re-enter the apparatus through the inlet G.

Hence the inventors claim that the employment of this process enables the walls of the container to be made of ordinary steel.

B.P. 289,759. *Catalyst tubes.*

L'Air Liquide. 1927. (See Fig. 238.)

This invention relates to processes for carrying out exothermic catalytic chemical reactions, and in particular to processes wherein the gases prior to reaction circulate in indirect contact with the catalysing material during which they become progressively heated, whilst any additional heat they may require is supplied from an external source.

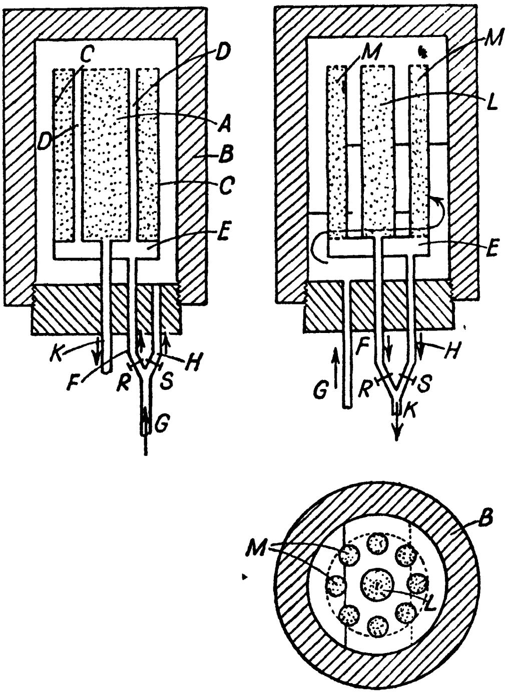


Fig. 238.—Catalyst tube for ammonia synthesis. (L'Air Liquide.)

It is known that in processes of this type, in order to obtain normal working, the surfaces through which the exchange of heat takes place should be adapted to the quantity of heat evolved in the tube containing the catalysing material per unit of time, and once the correct adjustment in this respect has been made for definite working conditions, these conditions can only be varied to a slight degree limited by the variations which may be obtained by varying the amount of heating from an external source or the temperature of the gases which are circulated in indirect contact with the catalysing material.

It has been recognised that under industrial conditions it was necessary to obtain a greater latitude in the operation of the catalysis tubes, and the present invention has for its object to provide a means which will permit of ensuring at all times the normal working of catalysis tubes in which there may occur important variations in the quantity of heat evolved by the reaction per unit of time, such variations taking place during the working and arising from variations in the concentration of certain reacting substances in the gases subjected to the process, variations in the quantity of the gases treated, variations in pressure, etc.

In the apparatus shown in the figure the receptacle or tube A containing the catalysing material is arranged as usual within a receptacle B, which if necessary is made pressure-resisting ; the tube A comprises an outer surface C as well as an inner nest of tubes D. The surfaces C and of the nest of tubes D may be partially heat-insulated. The gases which are to react, which may if necessary be previously heated, enter the apparatus through the pipe G, and can be separated into two parts, the one of which passes through the pipe H provided with the regulating valve S and enters the interior of the receptacle B, and circulates round the surface C, whilst the other passes through the pipe F, provided with the regulating valve R, and enters a chamber E, which distributes it into the nest of tubes D. These two gaseous streams again mix at the top of the receptacle B, and then pass over the catalysing material where the reaction takes place, finally leaving the apparatus through the pipe K. By way of example, there may be considered as a particular case for the application of the apparatus shown in (1) that of a variation in the amount of the gaseous substances which are to react. If the quantity of the gases treated is low, the valve R is closed and there is only utilised the exterior surface C of the tube A containing the catalysing material. If the quantity of the gases treated increases, then the valve R is opened, and the distribution of the gases passing through the valves R and S is regulated in such manner that the two streams of gas, after having circulated respectively around the surface C and through the nest of tubes D, and then become mixed, are at a temperature suitable for the reaction.

In the apparatus shown in (2) and (3), the catalysing material is disposed in a central tube L, the surface of which may be partially heat-insulated, and in a nest of tubes M exterior to the tube. The central tube L is connected with a gas outlet pipe F, provided with a valve R, and the nest of tubes M is connected through an intervening chamber E with an outlet pipe H provided with a valve S. The pipes F and H are finally connected by one common outlet pipe K. The gases which are to react enter the apparatus through the pipe G and by means of baffle plates suitably arranged are made to circulate simultaneously in contact with the surface of the nest of tubes M and the surface of the central tube L. Having reached the end of their course the gases divide into two parts regulated by means of the valves R and S, the one passing over the catalysing material in the tube L, and the other over the catalysing material contained in the tubes of the nest M. After reaction the gases leave the apparatus through the pipes H and F and become reunited in the pipe K. By way of example, there may be considered as a particular case for the application of the apparatus shown in (2) that of a variation of the concentration of certain reacting substances in the gases which may occur in the conversion into methane of carbon monoxide present in the gaseous mixture of nitrogen and hydrogen, it being assumed that the surface of the nest of tubes M permits, owing to a larger surface area or a higher heat conductivity or of the simultaneous effect of both these factors, of an exchange of heat notably greater than that afforded by the surface of the central tube L. If the concentration of carbon monoxide is high, say 2-3 per cent., for example, then the valve S will be closed, and the valve R will be opened; if, on the contrary, it is low, of the order of one-thousandth, for example, then the valve R will be closed and the valve S will be opened. For intermediate concentrations the valves R and S will be regulated in a suitable manner.

Instead of the single central tube L mentioned above, there may also be employed a group of tubes connected to the same outlet pipe F.

B.P. 289,823. *Catalyst tubes.*

L'Air Liquide. 1928. (See Fig. 239.)

This relates to improvements in processes for carrying out catalytic exothermic gaseous reactions, for example for effecting the synthesis of ammonia, and has for its object the improvement of the conditions of carrying out such reactions and to render the temperature more uniform throughout the whole of the catalysing material. The invention has particular reference to processes in which the gases which are to react circulate before reaction through a space or spaces in which they are in indirect contact with the catalysing material, and where they become heated by absorption of heat from the catalysing material.

According to this invention, it is stated to be advantageous to fill the space or spaces in question partially or wholly with catalysing material. In this way, if for any reason during the operation of the process the temperature of the gases circulating in such space or spaces reaches the temperature of reaction before they arrive in contact with the main portion of the catalysing material, these gases will have an opportunity of reacting immediately by reason of the presence of this additional portion of catalysing material.

Such an arrangement is also stated to render uniform the temperature in the catalysing material placed in the space or spaces above mentioned, that is to say, in the heat exchange device, on account of the greater velocity of the gases traversing this device, thus diminishing for this very reason the violence of the reaction; this greater velocity arises from the fact that generally the transverse section of the heat exchange device is smaller than that of the space occupied by the catalysing material in the apparatus previously used.

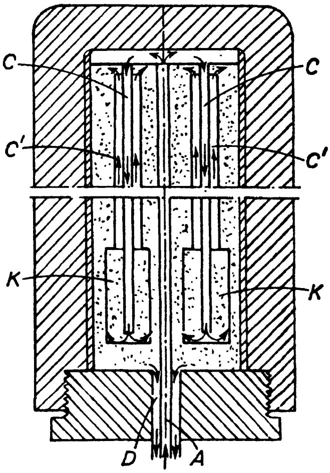


FIG. 239.—Catalyst tube for ammonia synthesis. (L'Air Liquide.)

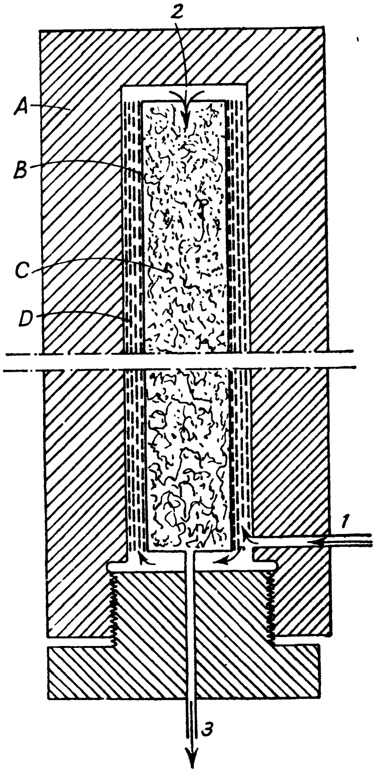


FIG. 240.—Catalyst tube for the synthesis of ammonia. (L'Air Liquide.)

In this apparatus the heat exchange device inside the catalysing material is constituted by the tubes C, C^1 arranged concentrically and provided at one of their ends with a part K in which some catalysing material is placed. The gases which are to react are admitted to the apparatus through the tube A and become heated during their passage through it by indirect contact with the catalysing material. The gases then pass through the interior of the tubes C and on to the catalysing material contained in the space K where they partly react, and which they leave before they reach too high a temperature. They then pass through the external tubes C^1, where they are cooled both by the gases circulating through the tubes C and by the main body of catalysing material which is at a lower temperature on account of being cooled by the gases entering through the tube A, which latter may be replaced if necessary by a plurality of tubes. After having arrived at the end of the tubes C^1, the gases come into contact with this main body of catalysing material and start reacting again. The gases pass through the main body of the catalysing material, and finally leave the apparatus through the annular conduit D. It must be noted that the arrangement of the first body of catalytic material K in the neighbourhood of the outlet conduit D has the advantage of avoiding too great a cooling of the gases during their circulation through the region towards the end of the main body of the catalysing material, thereby further conducing to rendering the temperature uniform.

Instead of two tubes, C, C^1, one inside the other, there may be used U tubes, the tube C^1 being then a continuation of the tube C, and the bent part of their junction being filled with catalysing material.

B.P. 307,840. *Catalytic apparatus.*

Soc. L'Air Liquide. March, 1928. (Fig. 240.)

In catalytic apparatus of the kind in which the reaction gases are circulated in a space D surrounding the catalyst chamber B this space is filled with a material of discontinuous structure such as metal gauze in order to assist heat transmission.

Casale Synthetic Ammonia Process.

The Casale synthetic ammonia process, like the Claude, is notable for the high working pressure, which in the case of the Casale plant is 750 atms. The following account of the Casale plant at Ostend is typical of Casale installation. The plant was built for the Union Chimique Belge, and an account of the Linde hydrogen-nitrogen installation at this works was given in Chapter III.

This account of the Ostend Casale plant appeared in *Industrial and Engineering Chemistry* in January, 1929, and I am indebted to the editor of that journal and also to the U.C.B. for permission to reproduce it.

At Ostend there were at first three 8-ton Casale units, and by the latter part of 1928 there were seven units. In the new plant then being planned by the U.C.B., 30-ton units were contemplated, although a unit of this size had not by that time been built.

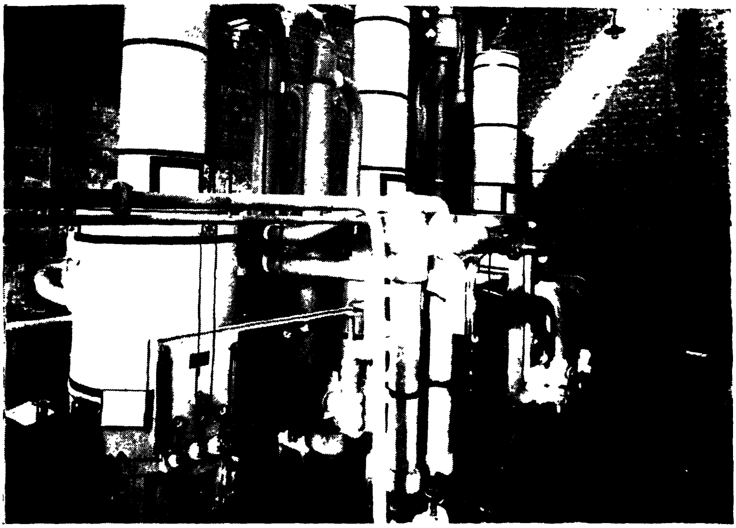
It having been thought in many quarters that it is advantageous to carry out the synthesis of ammonia at lower pressures, the

U.C.B. point out that the use of very high pressures has many decided advantages. One of the most important is that the entire ammonia output is available in the form of liquid ammonia, the latent cold of which is extremely useful, and permits very considerable energy savings in other parts of the plant, especially where coke-oven gas has to be treated. The elimination of the huge refrigerating machines, which would be required in the absence of available liquid ammonia, alone constitutes a considerable economy of energy, as has been mentioned in the description of the coke-oven gas treatment (see Chap. III.). The availability of the total output in the form of liquid ammonia also renders complete removal of benzene possible without any appreciable energy consumption, and besides, there are still other uses of this liquid ammonia in the modern ammonia derivatives plant, such as refrigeration of the nitrous fumes in the ammonia oxidation nitric acid plant, etc., which made the liquid state of the Casale ammonia an extremely valuable asset to the process.

As regards power consumption in compressing the gas, it has been repeatedly shown that there is very little difference in the energy consumed once the pressure exceeds 200 or 300 atms. For instance, the ratio of the energies required for compressing an ideal gas to 729 and to 243 atms. is 6 to 5, so that, whereas the Casale process consumes 1·2 K.W.H. per kilogram of ammonia for compression, a process working under 300 atms. will still consume 1·05 K.W.H. This difference, small as it is, is compensated by the absence of a recirculating pump in the Casale cycle, recirculation being induced in the latter system by the injection of the fresh gas, under a drop of about 50 atms. pressure. (See Chap. II. for details.)

At Ostend the hydrogen-nitrogen mixture produced in the Linde hydrogen plant is sent to a gasholder, whence it is exhausted by the compressors. These compressors (there are six of them) each compresses 1200 cu. metres of hydrogen-nitrogen mixture per hour. The compressed mixture is admitted as such, without any purification or desiccation, into the synthesis cycle, which comprises an oil separator, a synthesis tube, a water-cooled condenser, and a condensate receiver. At Ostend recirculation is still being effected in most of the units by means of recirculation pumps, but these are being replaced by a new injector system which simplifies the circuit considerably, and does away with the upkeep and attendance, as well as power consumption, necessitated by these pumps (see Chap. II.).

Further simplifications have been brought in at the pioneer plant at Terni, which is run as an experimental plant by the Societa Italiana Ricerche Industriali Siri, this company being the research organisation of the Casale Company, and founded by Luigi Casale. These simplifications consist in the elimination of the oil separator



Linde nitrogen plant. Synthetic ammonia plant. (U.C.B., Ostend.)

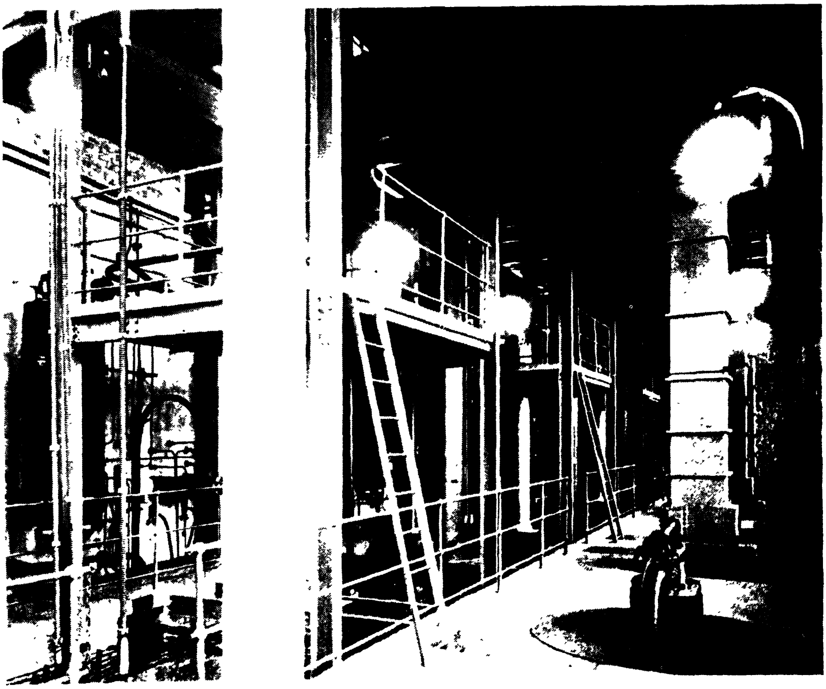


FIG. 241.—Synthesis tubes, ammonia condensers and receivers. Casale plant. (U.C.B., Ostend.)

[*To face page* 354.

(as a result of the suppression of the recirculation pumps) and the incorporation of water-cooled ammonia condenser and condensate receiver into one single apparatus. The two 5-ton units working under this system at Terni are very simple, and occupy the small space of 12 × 30 ft. for the two compressors.

Compressors at Ostend have been modified in order to be able to receive their hydrogen as it comes directly under the pressure of 9 atms. from the Linde fractionating apparatus. This arrangement permits of a further energy saving amounting to one-third of the compression energy, so that the power requirement is reduced from 1·22 to 0·82 K.W.H. per kilogram of ammonia in the 6-ton units, and to 0·76 K.W.H. in the 20-ton units.

An interesting feature of the Casale system is the catalyst tube, which is so arranged that the pressure tube, which is very similar to a big naval gun, is kept at a temperature at least 100° C. below the temperature at which the alteration of the structure of the metal under the effect of hydrogen begins. The efficiency of the Casale design is shown by the fact that a catalyst tube, which has been in continuous action for six years, was tested at 1500 atms. and withstood the test.

This result is achieved by so directing the gases inside the tube that the inside surface of the pressure tube will be cooled by the incoming cold gaseous mixture, which in the course of its progress takes up part of the heat of the hot gases as they leave the catalyst. The catalyst is contained in an annular space in the core of the tube, and is thermally insulated from the inside wall of the pressure tube by the concentric heat exchanger and the cold gas which enters the tube. This arrangement is protected by several Casale patents.

The reaction is regulated in the following manner: As under 750 atms. pressure the violence of the catalytic reaction would be such as to overheat the catalyst, there is left in the reaction mixture sufficient uncondensed ammonia to keep the system just slightly endothermal, so that it may be regulated by means of an electrically heated resistance placed in the axis of the catalyst tube, and over which the gases pass just before entering the catalyst, after they have been heated by temperature exchange with the gases which leave the catalyst. In practice the voltage and amperage are kept constant, the speed of recirculation being regulated so as to maintain temperatures and regular production. The energy consumed by the resistance is from 0·27 to 0·18 K.W.H. per kilogram of ammonia.

The presence of the necessary quantity of uncondensed ammonia in the gaseous mixture before catalysis is insured by simply water-condensing the reaction gases.

The Casale Catalyst.

The process of catalyst manufacture, which has been patented, consists in burning steel turnings in oxygen, in the presence of certain activators which are introduced in the form of certain very cheap materials. The temperature at which the combustion in oxygen takes place is so high as to drive off any phosphorus or sulphur. When all the metal is burned and the oxide solidifies, the mass is allowed to cool, and is then broken up and crushed into pieces of a proper size. The catalyst is introduced in the form of an oxide, and is reduced in the catalyst tube by means of hydrogen-nitrogen mixture.

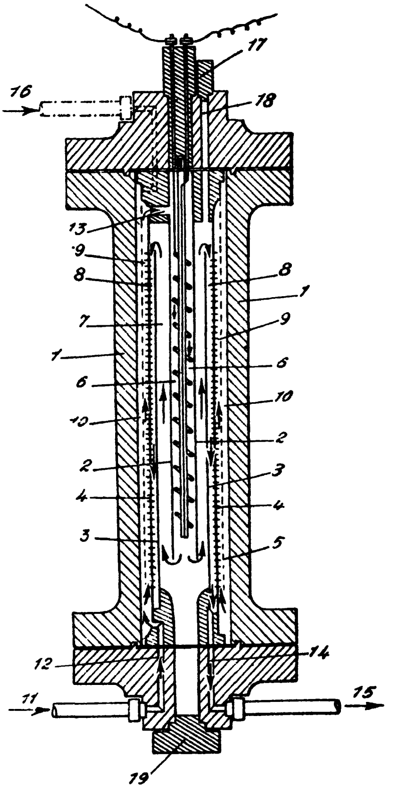


FIG. 242.—Catalyst tube.
(L. Casale, 1925.)

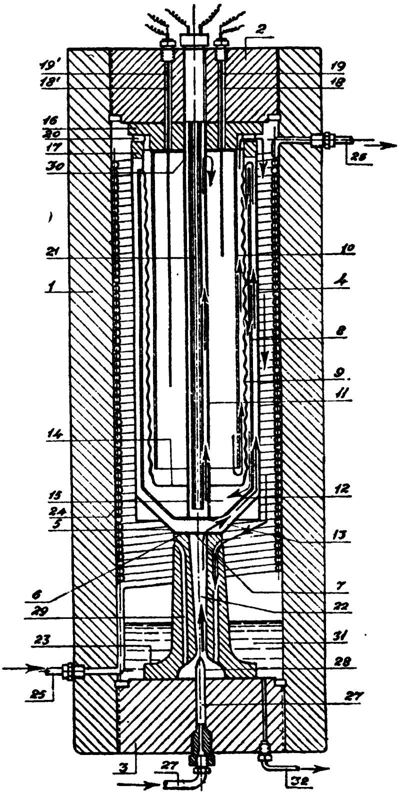


FIG. 243.

The following patent by L. Casale is of interest in connection with his technique in regard to the synthesis of methyl and higher alcohols :—

B.P. 252,713. *Catalytic apparatus.*

L. Casale. May, 1925. (See Fig. 242.)

In the production of ethyl, methyl and higher alcohols and other oxygenated organic compounds by the catalytic interaction of oxides of carbon and hydrogen, the reaction gases are preheated by the hot reaction products in the same apparatus that contains the catalytic chamber. The apparatus comprises a pressure tube (9) and a tube (2) containing an electric heater between which two tubular partitions (3) and (4) are placed, the space between (2) and (3) being filled with catalytic material.

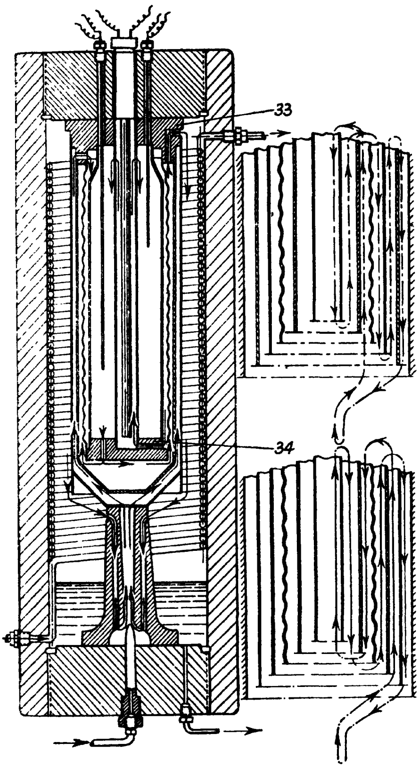


Fig. 244.—Catalyst tubes.
(M. C. Sacchi, 1929.)

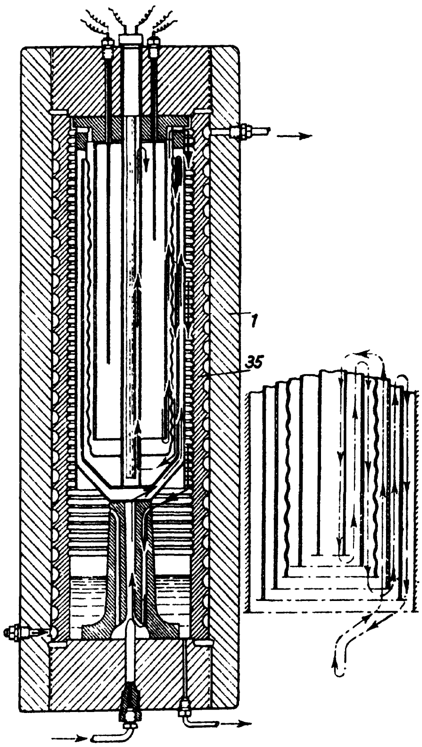


Fig. 245.—Catalyst tubes.
(M. C. Sacchi, 1929.)

The gases entering by passages (11) and (12) pass into the space (9) between the tubes (1) and (4), and thence through the passage (13) into the space (6), in which any deficit of heat is made up from the electric heater; after flowing through the catalytic material, they traverse the space (8) between tubes (3) and (4), where they surrender their heat to the ingoing gases flowing in the adjacent space (9), and are then discharged through passages (14) and (15). The surfaces of the tubes (2) to (4) may be ribbed to facilitate heat exchange.

Several interesting suggestions in connection with reaction vessels for the synthesis of ammonia, methanol, etc., are contained in B.P. No. 328,139 of 1930 granted to M. C. Sacchi. Figs. 243, 244, 245 and 246 of the patent specification give details of these suggestions.

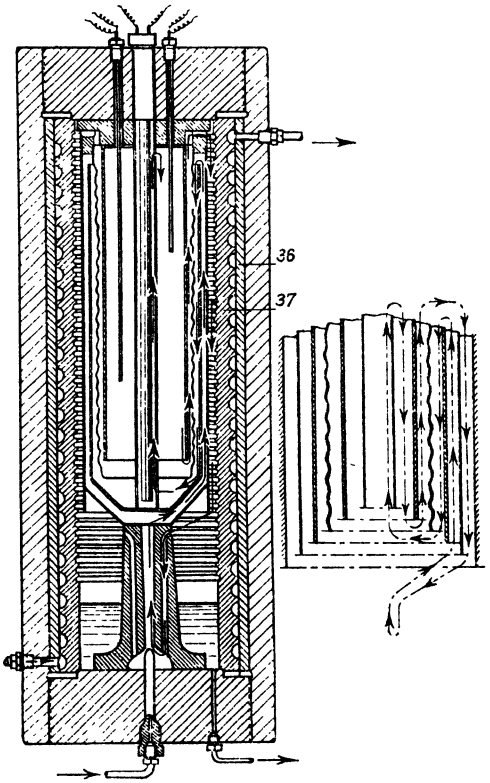


Fig. 246.—Catalyst tubes.
(M. C. Sacchi, 1929.)

B.P. 328,139. *Catalytic apparatus.*

S. G. S. Dicker (Sacchi, M. C.). May, 1929.

Apparatus for the execution in closed circuit of catalytic reactions between gases under pressure and at high temperature comprises in a single unit device for heating the reacting gases passing them through the catalyst, recovering heat from the reacted gases, cooling the latter, separating the products and continuously circulating the reacting gases by means of an ejector.

In the illustrated apparatus (Fig. 243) the gases coming from the compressor, mixed with a suitable quantity of gases already contained within the apparatus, pass first through the space between the tubes 5 and 12, and then through the annular spaces between 4 and 8, 8 and 9, and 12 and 14. Through holes 15 the gases enter tube 11 in which is placed an electric heating device. The heated gases leave this tube through holes 30, placed in the upper end of tube 11, and thence through the catalyst which is contained in the annular space between 10 and 11.

The gases then pass between tubes 9 and 10 (see directional arrows), and passing through the space between tube 4 and the walls of the catalyst vessel 1, are cooled to a suitably low temperature by fluid flowing through this cooling coil. Condensable products in the gas stream are collected in space 31, whence they are drawn off through pipe 32. The remaining unconverted gases are then drawn into the apparatus again through pipe 29, by the injector action of the fresh incoming more highly compressed gas. (See Fig. 51, Chap. II., for details of Casale injector device for recirculation.) The various heat interchange tubes within the apparatus are ribbed as shown to assist heat transfer. Fig. 244 shows a variation of the above design, and Figs. 245, 246 show two different ways of arranging the cooling part of the apparatus.

Imperial Chemical Industries Ltd.

Imperial Chemical Industries Ltd. (which has absorbed Synthetic Ammonia and Nitrates Ltd.) have also taken out numerous patents in connection with reaction vessels for high-pressure processes.

In regard to the ammonia process, for example, the company were granted B.P. No. 248,999 of 1925, which is as follows :—

B.P. 248,999. *Catalyst tubes.*

Synthetic Ammonia and Nitrates Ltd., and F. H. Bramwell.

In a process, for example, for carrying out the synthesis of ammonia, a heat exchanger is used, comprising a plurality of thermally insulating cylindrical baffles C.D. forming annular spaces (1-5), containing a large number of small cross-section tubes (6), extending parallel to the axis of the apparatus up and down within the annuli ; and connected so that the gas flows through them in parallel. (See Figs. 247 and 248.)

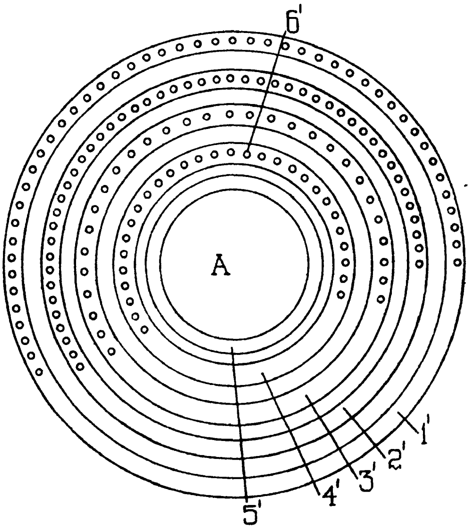


FIG. 247.—Catalyst tubes. (Synthetic Ammonia and Nitrates Ltd.).

In the same year, Synthetic Ammonia and Nitrates were also granted B.P. No. 255,963 in connection with heat exchange in ammonia reaction vessels, and which was as follows :—

B.P. 255,963. *Catalyst tubes.*

Synthetic Ammonia and Nitrates Ltd., and H. A. Humphrey. 1925.

In carrying out exothermic reactions between gases such as the synthesis of ammonia, with the use of catalysts, the direction of flow of the gases relative to the catalyst is periodically reversed, whereby the temperature of the catalyst is maintained more nearly uniform. In connection with above see also E.P. 255,964.

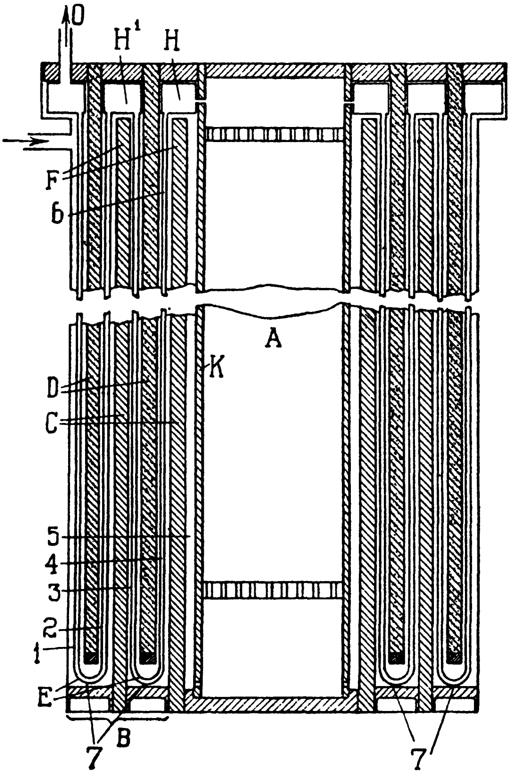


FIG. 248.—Catalyst tubes. (Synthetic Ammonia and Nitrates Ltd.)

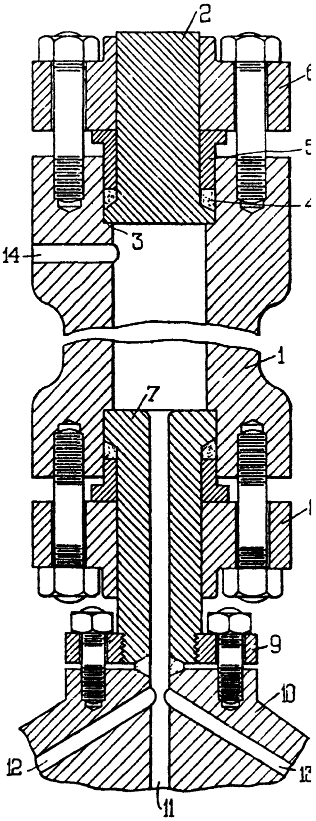


FIG. 249.—High-pressure chemical reaction vessel. (Imperial Chemical Industries, 1927.)

Other English patents granted to this company in connection with high-pressure plant are as follows :—

B.P. 309,258. *High-pressure apparatus.*

Synthetic Ammonia and Nitrates Ltd., and Rule. 1927. (See Fig. 249.)

Apparatus for carrying out reactions between gases and liquids at high-pressure comprises a tower very long in proportion to its width, into which the liquid and gas are introduced at the lower end, and from which the product is withdrawn at the upper end. The apparatus is suitable for the destructive hydrogenation of carbonaceous materials at a pressure over 300 atms. In the illustrated apparatus the liquid materials are introduced at (11), and hydrogen at (12), (13), and products are withdrawn through the opening (14).

NOTE.—This apparatus shows another variation of Bridgman's "unsupported area" method of securing fittings and covers to a pressure vessel. In this case the internal pressure acting on the whole area of the end plug produces a greater pressure *intensity* in the jointing material 4.

B.P. 311,193. *Separating liquids and gases under high pressure.*

C. Harrison and Imperial Chemical Industries Ltd. December, 1927. (See Fig. 250.)

Gases and vapours are separated from liquids contained in admixtures, which are the product of high-pressure reactions, such as destructive hydrogenations at the reaction pressure and at a temperature high enough to prevent condensation of the vapours. The gas after cooling and/or scrubbing to remove condensable vapours may be expanded in an engine, and the liquid, after cooling, may be utilised to drive a Pelton wheel. The liquid and gas from a converter (1) are separated in a separator (3), the liquid passing through the discharge valve (5) through a heat exchanger (4), and the gas to a heat exchanger (7) in which benzine vapours are condensed and collected in a catch pot (8), from which gas issues through a valve (10) and benzine through a valve (9).

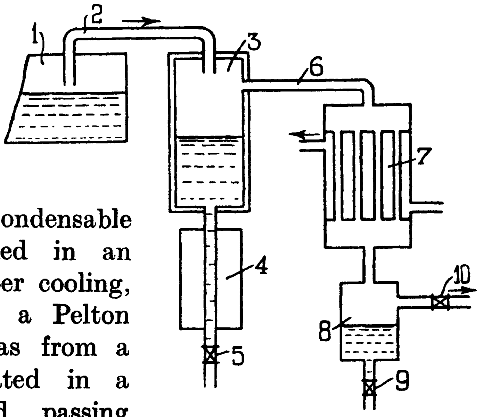


FIG. 250.—Method of separating gases and liquids under high pressure.
(Imperial Chemical Industries, 1927.)

B.P. 317,131.

Gordon and Imperial Chemical Industries. May, 1928. (See Fig. 251.)

In processes for carrying out reactions between gases at high temperatures and pressures, e.g. the synthesis of ammonia and methanol, the gases are heated by passing through a pressure vessel within which is a bath of molten lead (5). The gases are bubbled through the lead and are kept from the pressure-resisting walls of the vessel (1), as shown in the figure by a baffle (4) depending into the liquid.

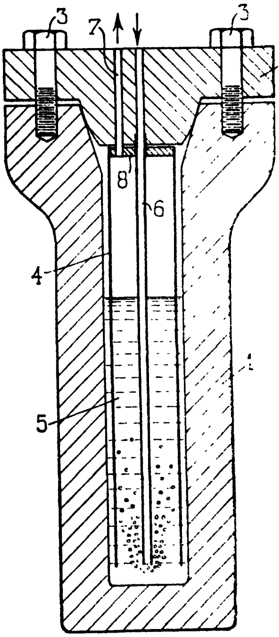


FIG. 251.—High-pressure reaction vessel.
(Imperial Chemical Industries, 1928.)

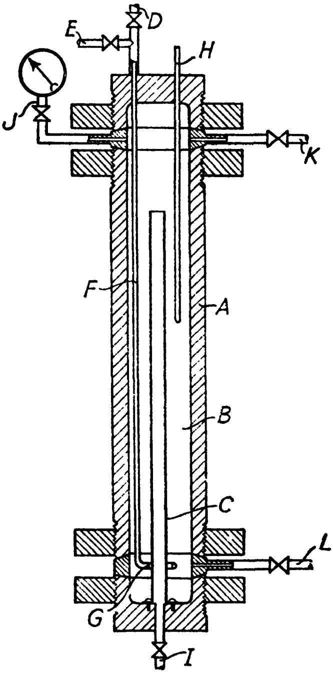


FIG. 252.—High-pressure chemical reaction vessel.
(Imperial Chemical Industries, 1929.)

B.P. 335,567. *High-pressure apparatus for chemical processes.*

Imperial Chemical Industries, and K. H. Saunders. March, 1929. (See Fig. 252.)

Reactions are carried out continuously in the liquid phase under increased pressure by introducing the liquid or liquids under treatment into a reaction chamber, whence on completion of the reaction the liquid overflows into a second chamber disposed in the reaction chamber and is drawn off. Thus, to prepare mercaptobenzothiazole equal volumes of carbon disulphide saturated with sulphur and aniline are pumped through tubes E and D, and mix in F to enter the pressure sustaining vessel "A" heated to 200-275° C. The reaction is completed by the time the mixture rises to the top of the tube C, into which it then overflows and is withdrawn through the valve I.

B.P. 364,215. *Catalytic gas reactions.*

Imperial Chemical Industries, and E. H. Sale. October, 1930.

In carrying out catalytic gas reactions at an elevated temperature, the reactants are separately preheated by heat exchange with different portions of the reaction product; the extent to which each reactant is preheated being independently controlled by regulating the amount of reaction product with which it is in contact, preferably by a valve on the cold side of the heat exchanger. The process is applicable to the catalytic hydrogenation of organic compounds, e.g. for the production of low boiling hydrocarbons by the catalytic hydrogenation of middle oil (boiling at 200-300°) obtained by the destructive hydrogenation of coal, in which case the hydrogen entering the reaction chamber is preheated in two stages to 550° C. before mixing with the oil vapours in the catalyst bed at temperatures of 470° C.

An interesting patent for a high-pressure process is B.P. No. 337,053, granted in 1929 to British Celanese Ltd., and which is as follows :—

B.P. 337,053. *Catalytic high-pressure apparatus.*

British Celanese Ltd., and W. Baden.

In an apparatus (see Fig. 253) for obtaining aliphatic acids and their esters by reacting, a mixture of liquid aliphatic alcohol and an acid catalyst with carbon monoxide at 200-450° C., and at pressures up to 300 atms. methanol from vessel (5), is mixed with phosphoric acid in a steam-jacketed chamber (1) at 60-90° C., and then passed to a jet (11). Carbon monoxide and steam are introduced into a preheater (12) by pipes (13) and (14) respectively, and pass to a gold or graphite lined reaction tube (2), heated electrically to 300-400° C., carrying with them methanol from the jet. The reaction products pass to a separator (15) where phosphoric acid separates and is returned to the mixing chamber (1). Volatile products are condensed in a condenser (17), and remaining vapours are absorbed in charcoal in a tower (19). The gas is then passed through a pump (3) for recirculation.

In this connection the following Badische Anilin English patent is of interest :—

B.P. 254,819. *Oxygenated organic compounds.*

Badische Anilin und Soda Fabrik. March, 1925.

Organic compounds containing oxygen are obtained by the reaction at high pressure and temperature of carbon monoxide or gases containing it upon a vaporised aliphatic alcohol or ester or mixture thereof in presence of hydrating catalysts or hydrating and hydrogenating catalysts. A mixture of carbon monoxide and hydrogen may be passed at high temperature and pressure over a methanol forming catalyst and the resulting gas mixture containing methanol vapours then treated with carbon monoxide.

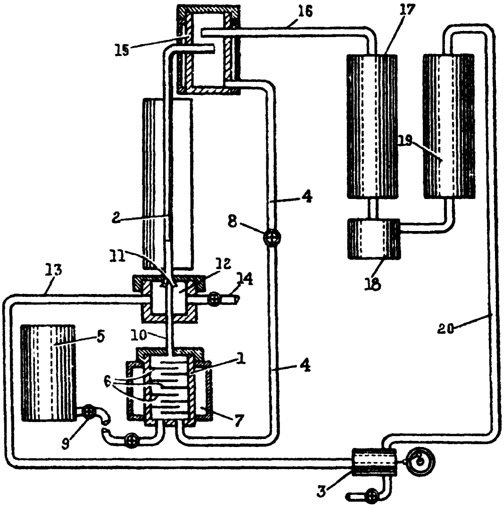


FIG. 253.—Catalytic high-pressure apparatus. (British Celanese Ltd.)

Among the suitable hydrating catalysts suggested are oxides of titanium, zirconium, vanadium, chromium, etc. As hydrogenating catalysts copper, silver, iron, nickel, cobalt, etc., are mentioned.

According to examples, methanol vapour and carbon monoxide are passed over a mixture of iron and manganese oxides, the resulting product containing butyric and valeric acids ; ethyl alcohol vapour and carbon monoxide are passed over a chromium oxide, manganese oxide catalyst giving products boiling at 100-250° C., including aldehydes, acids, esters and alcohols.

A British patent granted to Professor G. T. Morgan and myself in 1930 in connection with the heating of high-pressure vessels is as follows :—

B.P. 325,678. *High-pressure chemical apparatus.*

G. T. Morgan and H. Tongue. (Fig. 254.)

High-pressure reaction vessels, e.g. for ammonia and methanol synthesis, are provided with heating or cooling means adjustably positioned in the interior of the vessel but externally accessible so that removal or adjustment can be effected without releasing pressure in the vessel. Fig. 1 shows a vessel provided with externally open tubes extending inwardly from one end plate of the vessel. An electric heating element (5) is adjustably fitted within each tube. In a modification the elements are replaced by tubes through which heating or cooling fluid is admitted to the tube (8), the inner tubes being slidable in order to vary the depth to which the fluid penetrates.

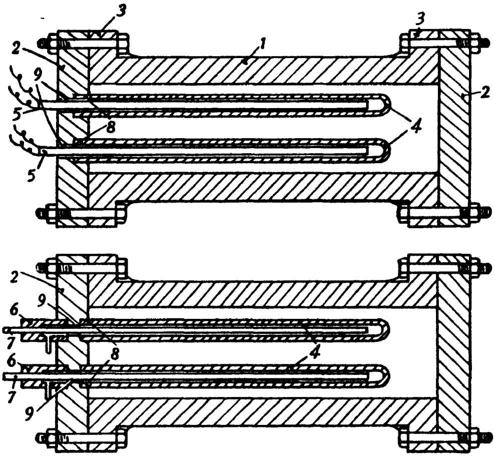


FIG. 254.—Method of heating catalyst tubes.
(G. T. Morgan and H. Tongue, 1930.)

An English patent granted to the company responsible for the development of the Mont Cenis process is of interest in connection with the attack by hydrogen of the metal walls of reaction vessels.

B.P. 307,027. *Catalytic apparatus for ammonia synthesis.*

Gasverarbeitungs Ges. March, 1928.

In order to avoid weakening of the structure of apparatus for reactions in which hydrogen at a high temperature is employed, hydrogen is heated in a heat exchanger in counter current with an inert gas such as nitrogen. Preliminary heating of the cold gases to a temperature not greater than 400° C. is attained by heat exchange with the gases from the reaction.

The Hydrogenation of Oils.

The following three British patents granted recently to the Standard Oil Company are included to show the trend of technique in the hydrogenation of oils, the yields obtained and suggested catalysts.

B.P. 340,811. *Destructive hydrogenation.*

Standard Oil Development Co. January, 1930. (See Fig. 255.)

In the destructive hydrogenation of fluent carbonaceous materials such as petroleum, tars, etc., a portion of the reaction mixture is withdrawn from the reaction vessel and the pressure of this portion is reduced so that a substantial part of the hydrocarbon liquid is distilled. Oil or the like, heated in a pipe still (1) passes to the reaction drum (3), from which a part of the oil is continuously recycled by a pump (6) back to the pipe still. Hydrogen is pumped by a compressor (8) into the still through valve (11) and into the reaction drum through valve (12). Vapours pass from the drum to a heat exchanger (15) and condenser (16). Hydrogen purified if necessary from hydrogen sulphide and gaseous hydrocarbons is returned by pump (18) to the pipe (10). A part of the reaction mass is withdrawn by a pipe (19) through a pressure reducing valve (20) to a vaporising chamber (21); solid residues are discharged through a

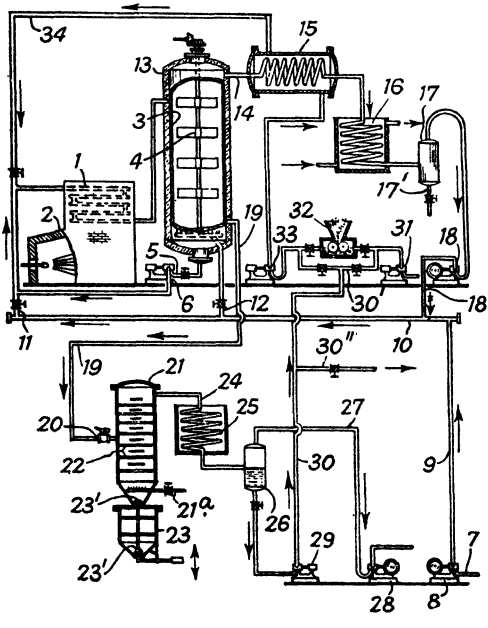


FIG. 255.—Destructive hydrogenation. (Standard Oil Co., 1930.)

double bell closure (23), and vapours are passed through a condenser (25) to a gas separator (26). Inert gas may be introduced through a valve (21*a*). Fresh oil is introduced into the system by pump (31), (33), through the preheater (15) and the pipe (34). Carbonaceous solids may be added from a pulverizer (32), and oil from the separator (26) may be recycled through pump (29).

B.P. 348,889. *Destructive hydrogenation.*

Standard Oil Co. May, 1930. (See Fig. 256.)

In a two-stage process for obtaining oils of low boiling-point from heavy oils, the oils in the first stage are destructively hydrogenated in the liquid phase at relatively low temperatures, e.g. 750-925° F., and under 50-100 atms. pressure, and the fractions so obtained are divided into fractions of low and intermediate boiling fractions. The intermediate fraction is treated again in a second stage into low boiling products rich in aromatic constituents by heating them in the vapour phase at high temperature, e.g. 850-1000° F. Crude oil is purified through preheating coils (1) and a reaction drum (3) supplied with hydrogen from a compressor (8) and lines (7-10). The vapours produced pass to a fractionating tower (13), from which the low boiling fractions pass to a condenser (16) and separator (17). The intermediate fractions condensed in the tower (13) are delivered through a pipe (22) to a second stage comprising a heating coil (24) and a vapour phase reaction drum (25), filled with catalytic material, and supplied with hydrogen from a heater (30). The products evolved are passed through an exchanger (29), where they are cooled by the hydrogen, to a fractionating tower (31), where the heavier fractions are condensed and returned to the coil (24) by a pump (23), while the lighter fractions pass on to a condenser (32),

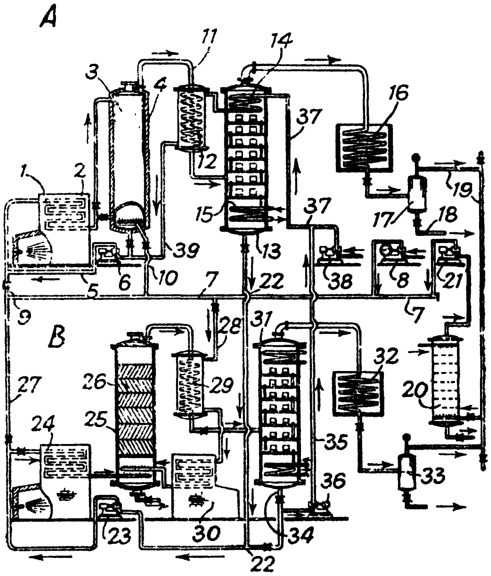


FIG. 256.—Destructive hydrogenation. (Standard Oil Co., 1930.)

and are separated from the hydrogen in a separator (33). The light fractions from each stage of the process are preferably blended to give a motor fuel having good antiknock properties.

B.P. 348,834. *Lubricating oils.*

Standard Oil Development Co. April 11th, 1930.

In preparing lubricating oils by hydrogenation of impure heavy oils, such as a heavy asphaltic base oil, the non-crystalline gummy, resinous or asphaltic impurities are first removed and the purified oil is treated with a gas rich in free hydrogen at high pressure, e.g. over 100 atms. at a temperature above 700° F., at which decomposition is relatively slow, e.g. below 800° F. With a heavy cylinder oil, the production of light oil boiling below 400° F. is less than 15 per cent., and may be as low as 5 per cent. A catalyst may be used, preferably one immune from sulphur poisoning, e.g. molybdenum or chromium oxide. The hydrogen consumed is about 300 cu. ft. per barrel, but this gas is used in considerable excess, e.g. over 3000 cu. ft. per barrel.

The Hydrogenation of Coal, Coal Tar, Oils, etc.

The following British patents are included to show the activity of the large chemical organisations in connection with the hydrogenation of coal, etc., to produce motor spirit and lubricating oils.

B.P. 249,155.

I.G. Farbenindustrie, A.G. March, 1925.

In the production of oils, etc., from coal, tars, mineral oils, etc., by treatment at high pressures and temperatures, with reducing gases containing hydrogen and carbon monoxide in the presence of catalysts, the hot parts of the apparatus in contact with the gases are made of metal not reacting with carbon monoxide. Metal carbonyl vapours are removed from the gases before use. Suitable metals are copper, vanadium, uranium, etc., or the corresponding alloys of nickel or cobalt containing a considerable proportion, e.g. 10-20 per cent. of manganese, titanium, chromium, tungsten, vanadium or molybdenum.

B.P. 249,501.

I.G. Farbenindustrie, A.G. March, 1925.

Benzine-like hydrocarbons are produced from crude mineral or shale oils, etc., by hydrogenation in presence of molybdenum or its compounds. In an example, Mexican asphalt is dissolved in an equal weight of cyclohexane and passed continuously at 200 atm. and at 450-500° C., with an excess of a mixture of 1 part of nitrogen with 3 parts of hydrogen (by volume) over a contact mass prepared by pressing into lumps a mixture of 10 lbs. of ammonium molybdate with 30 lbs. of aluminium hydroxide.

B.P. 269,521.

I.G. Farbenindustrie, A.G. April, 1926.

Hydrocarbons are obtained by passing oxides of carbon with hydrogen at elevated temperature and pressure over catalysts containing metallic sulphides at pressures not exceeding 50 atms. Parts of the apparatus which come into contact with the heated gases should be free from iron. According to an example, an oil resembling petroleum is obtained by circulating water gas at a pressure of 20 atms., through an aluminium-lined chamber charged with cobalt sulphide and heated to 270° C.

B.P. 345,305. *Destructive hydrogenation.*

H. W. Strong and Imperial Chemical Industries. December, 1929.

Catalysts for the destructive hydrogenation of carbonaceous materials comprise cobalt or nickel alloyed with and/or coated with tin. Suitable alloys comprise cobalt-tin, nickel-tin, iron-nickel-tin, iron-cobalt-tin, nickel-cobalt-tin, and these alloys may be employed in the powdered or massive state, and may be coated with tin.

An example of the efficacy of this catalyst is as follows :—

Middle oil obtained in a liquid phase destructive hydrogenation is fed in the vapour phase at the rate of 2 kg. per hour along with hydrogen at 3·5 cu. metres per hour into a vertical reaction vessel packed with rings of a nickel-iron alloy coated with tin, the materials being treated for two mins. at 470° and 250 atms. ; 37·5 per cent. of the middle oil is converted into petrol boiling below 200° C. in one operation, rising to 70 per cent. by recycling the unconverted residues.

B.P. 349,892. *Destructive hydrogenation.*

I.G. Farbenindustrie, A.G. March, 1930.

Residues obtained after refining heavy mineral oils, tar oils, etc., with alkalis are treated by destructive hydrogenation in the presence or absence of catalysts to produce products of a lower boiling-point. The pressures employed may be between 5-1000 atms. at temperatures of 300-700° C. The catalysts used are compounds of the sixth group of the periodic table, e.g. oxides of molybdenum, tungsten or chromium or cobalt sulphide.

B.P. 358,180. *Catalysts for hydrogenation of carbonaceous materials.*

Naamlooze Vennootschap de Bataafsche Petroleum Maatschappij. July, 1930.

Colloidal rhenium, or compounds of rhenium in colloidal form on suitable carriers, are used in the treatment of carbonaceous materials at high temperatures and pressure in the presence of hydrogen for effecting destructive hydrogenation. The starting material may be coal, lignite, asphalt, tars, tar fractions, etc.

In the example, cresol was heated to 450° C., from room temperature, for forty mins., with hydrogen at about 100 atms. initial pressure in presence of colloidal rhenium sulphide on active carbon. Heating was stopped and the pressure was released while the temperature was between 320° and 250° C. The product contained 41·4 per cent. gasoline, boiling mainly below 110° C.

B.P. 362,354. *Purifying oils and asphalts. Destructive hydrogenation.*

Naamlooze Vennootschap de Bataafsche Petroleum Maatschappij. 1930.

Colloidal rhenium, or compounds of rhenium in colloidal form on suitable carriers, is used as a catalyst in treating carbonaceous materials at high temperatures and pressures in presence of hydrogen for effecting destructive hydrogenation. In the example, a light motor oil is heated with hydrogen at 100 atms. to 430° C., in the presence of a colloidal rhenium molybdenum catalyst on active carbon. On release of pressure, 86 per cent. of a lubricating oil remains in the autoclave, and the vapours yield 11·5 per cent. of distillate; 19 per cent. of the total sulphur remains in the liquid products. The catalyst is prepared by adsorbing colloidal molybdenum oxide and colloidal rhenium sulphide respectively on carbon, and 3 parts of the molybdenum mass containing the equivalent of 3·75 grams MoO_3 are used with 2 parts of the rhenium mass containing the equivalent of 0·9 grams ReS_2.

B.P. 358,495. *Lubricants, cracking hydrocarbons.*

I.G. Farbenindustrie, A.G. May, 1930.

Lubricating oils are produced by condensing or polymerising liquid olefines obtained from saturated aliphatic compounds, together with paraffinic hydrocarbons in the presence of a condensing agent. As the paraffinic hydrocarbon component, tars, mineral oils, etc., may be used. During condensation gaseous olefines such as ethylene may be passed in under pressure.

The liquid olefines preferably contain more than 5 carbon atoms, and may be produced by strongly cracking solid paraffins or oils at 450-500° C., under elevated pressure in the presence of methane.

BP. 368,373. *Motor fuels. Catalysts, aluminium hydroxide.*

I.G. Farbenindustrie, A.G. December, 1930.

Motor fuels are rendered antiknocking by the addition of iron carbonyl and an amine prepared by passing a crude phenol and ammonia over a dehydrating catalyst such as aluminium hydroxide at pressures above atmospheric and temperatures above 400° C.

B.P. 374,567. *Destructive hydrogenation, catalytic processes.*

Chemical Reactions Ltd. April 10, 1931.

Carbonaceous materials such as tars, oils, naphthalene are hydrogenated at elevated temperatures and pressure in the presence of iron, cobalt or nickel, or their compounds with sufficient hydrogen sulphide to produce a greater yield than would be obtained by using only the sulphides of these metals as catalysts. In hydrogenating naphthalene, the reaction may be carried out below about 480° C., producing tetra- and deca-hydronaphthalenes, or above about 500° C., in which case the ring is split into benzene hydrocarbons.

B.P. 379,335. *Catalytic agents and processes.*

I.G. Farbenindustrie, A.G. May, 1931.

Catalysts suitable for use in reactions involving carbonaceous materials, especially destructive hydrogenation, comprise metal sulphides other than iron sulphide which are prepared from metals or their compounds, especially from groups 5-6 of the periodic system, under vigorously sulphidizing conditions, i.e. by treatment with liquid or vaporous sulphur or volatile compounds containing divalent sulphur under conditions allowing an intensive reaction or by the thermal decomposition of thio salts.

Details of the preparation of catalysts are given.

B.P. 379,587. *Destructive hydrogenation, purifying mineral oils, catalytic agents.*

International Hydrogenation Patents Co. Ltd. December, 1931.

Catalysts for the production of hydrocarbons by reaction of hydrogen upon carbonaceous materials such as naphthalene, coal, wood, oil, etc., and for the refining of crude benzol, etc., are prepared by mixing a solution in water, alcohol, etc., of a metal compound with an adsorbent such as active carbon, pumice, broken pottery, etc., and treating the mixture so as to yield a metal or metal compound which is insoluble and becomes adsorbed. Preferably metal compounds are used which are immune to sulphur poisoning such as compounds of metals of the sixth group, particularly molybdenum and tungsten.

Manufacture of Methyl Alcohol, etc., from Mixtures of Carbon Monoxide and Hydrogen.

The following British patents are interesting in connection with the manufacture of methyl and higher alcohols from mixtures of carbon monoxide and hydrogen.

B.P. 247,932.

G. Patart February, 1925.

A catalyst for the treatment of a mixture of water gas and coal distillation gas at elevated temperature and pressure to produce a mixture of methyl alcohol and hydrocarbons is prepared by reducing agglomerated basic chromate of zinc.

B.P. 250,563.

G. Patart. April, 1925.

A catalyst for the production of higher alcohols by interaction of carbon monoxide and hydrogen at elevated temperature and pressure comprises a mixture of the common methanol forming metallic oxides and a combination of an alkali or alkaline earth oxide with a metallic oxide of an acid character, e.g. chromates, manganates, molybdates, tungstates, uranates and vanadates of sodium, potassium, rubidium, and barium.

B.P. 275,345.

Synthetic Ammonia and Nitrates Ltd., and H. G. Smith. May, 1926.

A catalyst for the production of methanol and other oxygenated compounds by interaction of carbon oxides and hydrogen at elevated temperature and pressure comprises a basic zinc chromate of the composition 4ZnO, CrO_3. This catalyst, which becomes reduced during the operation, or may be reduced beforehand, is not poisoned by sulphur, though volatile compounds of iron, nickel and cobalt should be excluded. Comparative experiments using a catalyst of varying compositions of zinc and chromium oxides under standard reaction conditions are described.

B.P. 282,448. *Catalytic agents and processes.*

Consortium für Electrochemische Industrie Ges. December, 1926.

Ethyl alcohol vapour is passed under ordinary or raised pressure, and at a temperature of 400-500° C. over a catalyst consisting of metal oxides or hydroxides, such as barium oxide, magnesia, or lime or manganese oxide, or compounds such as magnesium or sodium alcoholates. The conversion products consist of higher alcohols such as butyl alcohol, acids, esters such as ethyl acetate, acetals, particularly diethylacetal, acetone and aldehyde.

B.P. 283,499. *Catalytic apparatus.*

Compagnie de Bethune. January, 1927.

In the process of the catalytic synthesis of methanol from carbon monoxide and hydrogen under high pressure, there is mixed with the reaction gases a liquid, e.g. water, the vaporisation of which will control the temperature of the reaction.

B.P. 287,846. *Catalytic agents and processes.*

Du Pont de Nemours & Co. March, 1927.

The conversion of primary alcohols other than methyl alcohol by passage of the vapours over a heated dehydrogenation catalyst is carried out under pressure whereby the formation of the ester of the acid corresponding with the alcohol is increased, an alcohol with twice the number of carbon atoms is obtained, and the production of the corresponding aldehyde and acid is diminished. Temperatures of 250-500° C. and pressures above 10 atms. may be used. In treating ethyl alcohol under a pressure of about 270 atms. at about 350° C., about one-half the alcohol is converted to a mixture of ethyl acetate, normal butyl alcohol and a small proportion of acetaldehyde. After condensation pure hydrogen remains.

The catalyst may consist of copper or nickel, cobalt or iron in admixture with other oxides, such as chromium.

B.P. 381,185. *Catalytic materials.*

British Industrial Solvents Ltd. June, 1931.

Catalytic materials for the preparation of higher alcohols from a mixture of methyl and ethyl alcohols in the presence of hydrogen comprise an alkaline earth metal oxide, particularly magnesia activated by the presence of less than 10 per cent. of one or more of the oxides of the metals lead, thorium, silver, uranium, tungsten, cadmium, tin, chromium, etc. The catalyst may be stabilised by the addition of aluminium oxide or hydroxide, titanium oxide or hydroxide, stannic acid gel, silica gel or wood charcoal.

The following miscellaneous British patents show other applications of pressure in connection with continuous catalytic processes :—

B.P. 367,892. *Catalytic apparatus. Dehydration of organic compounds.*

I.G. Farbenindustrie, A.G. November, 1930.

For the catalytic dehydration of organic compounds the catalyst is rigidly applied to the inner surfaces of the apparatus through which the heat necessary for the reaction is conducted from an exterior source. For example, the catalyst may be coated on the inner or outer surfaces of ribbed tubes. Specified reactions to which the invention is applicable are the conversion of hydroxy compounds such as isoamyl alcohol and 1 : 3-butylene glycol into unsaturated hydrocarbons such as isoamylenes and butadienes, of glycols into oxides, of alcohols and acids into esters. The reaction temperature may be 250-300° C., and reduced atmospheric or increased pressure may be employed. Specified catalysts are :—

(1) Monosodium phosphate and red phosphorus.
(2) Monosodium phosphate and aluminium hydroxide.
(3) Sodium metaphosphate and bauxite.

B.P. 342,068. *Nitric acid ; chemical apparatus.*

Caro and Frank. December, 1929.

Highly concentrated nitric acid is made by reacting oxygen or oxygen containing gases, water or aqueous nitric acid, and nitrogen oxides or liquid nitrogen tetroxide at temperatures above 70° C., and at pressures of the order of 50-200 atms.

The conduits, fittings and pressure chambers or their linings may be of alloys such as chromium steel ; aluminium or its alloys is also suitable, especially for the linings.

B.P. 384,714. *Catalytic agents.*

Du Pont de Nemours & Co. August, 1931.

A contact mass for the manufacture of amines from aliphatic alcohols and ammonia comprises a porous rigid gel impregnated with an oxide acting as a dehydrating catalyst.

In the examples (1) silica gel is evacuated at 400° C., cooled *in vacuo*, immersed in aluminium nitrate solution, dried and ignited at

400° C. (2) A contact mass comprising boron trioxide supported on silica gel is prepared, as in example (1) from silica gel and ammonium borate.

B.P. 273,622. *Dehydrogenated organic compounds, catalytic production of.*

H. Dreyfus.

Ketene is produced by subjecting acetaldehyde vapour to a relatively high temperature in the presence of a dehydrogenating catalyst such as nickel, copper or zinc. Preferably the reaction is carried out at 150-300° C., and at atmospheric pressure, but the temperature may attain 500° C., and pressures of 5-50 atms. may be applied.

B.P. 272,155.

Soc. Chimique de la Grande-Paroisse, etc. June, 1926.

Catalysts for use in the production of formaldehyde by the interaction of carbon monoxide and water or steam comprise magnesium, zinc, manganese, tin, lead, antimony and bismuth or their oxides or salts.

The walls of the reaction chamber are made of, or lined with, inert metals, aluminium or copper may be employed.

B.P. 363.344. *Catalytic dehydrogenation.*

I.G. Farbenindustrie, A.G. June, 1930.

In the conversion by heat treatment of paraffinic or olefinic hydrocarbons which are gaseous at ordinary temperature and pressure into hydrocarbons having a lower content of hydrogen, high temperature coke formed in the dry distillation of coals is used as a catalyst, the coke being heated up from time to time and then used as a heat accumulator supplying the heat required for the conversion. The catalyst may be partly or wholly freed from mineral constituents, especially from iron, by boiling up with acids before its employment. An example given is the conversion of ethane, propane or butane into aromatic hydrocarbons. Temperatures of 600-900° C. should be employed at ordinary pressures, while at elevated pressures between 50-200 atms. temperatures between 400° and 650° C. are preferable.

B.P. 371,555. *Facilitating chemical reaction by radiation.*

Soc. Française de Catalyse Généralisée. March, 1931.

Acetamide is obtained by causing hydrogen to react on formamide, or on a mixture of carbon monoxide and ammonia, under the influence of ultra-violet or infra-red radiations. The reaction between hydrogen and formamide takes place at ordinary pressure and temperatures between 200° and 500° C. In the case of carbon monoxide and ammonia pressures of at least 100 atms. and temperatures of 100-300° C. are used. Catalysts consisting of pumice stone, carbon powder, finely divided metals, particularly copper, or metal oxides such as aluminium oxide, may be present.

Synthetic Ammonia in the United States.

Regarding the development of high-pressure synthetic ammonia in the United States, perhaps the largest installation is that of the Du Pont de Nemours & Co., at Belle, West Virginia.

Originally this company started with a synthesis unit based upon the designs and experience of M. Georges Claude with an output of 25 tons of anhydrous ammonia per day. The company then acquired the exclusive American rights of the Casale process. The company has since carried out a long programme of technical research on this subject, and the present process at Belle represents a radical departure from the original Claude process.

The Du Pont Ammonia Corporation has found that in their case hydrogen can be made more cheaply from water gas than from coke-oven gas plants. An integral feature of the subsequent synthesis at 1000 atms. pressure is that methanol is produced by catalysis in the first synthesis tube at commercially productive rates by leaving a percentage of carbon monoxide in the hydrogen-nitrogen mixture.

I am indebted to the Du Pont de Nemours Co. for permission to reproduce four photographs of their synthetic ammonia plant at Belle, West Virginia (Figs. 257, 258, 259 and 260). Fig. 257 is a view showing the large compressors for compressing the crude water gas for separation into its various constituents. Fig. 258 gives a general view of the gas plant; the water-gas gasholder is in the background. The scrubbing towers for gas purification are in the left background, and the water-gas plant is in the right background. The tank cans for shipping anhydrous ammonia and methyl alcohol are in the right foreground. Fig. 259 shows the interior of the high-pressure synthesis building, with a view of the high-pressure converter and condensing equipment. Fig. 260 shows the high-pressure research laboratories of the Du Pont de Nemours Co.

In connection with the synthetic ammonia activities of the Du Pont Co., the following abstract of a letter from Mr. Jasper E. Crane of that company to Senator Norris of the U.S. Senate is of

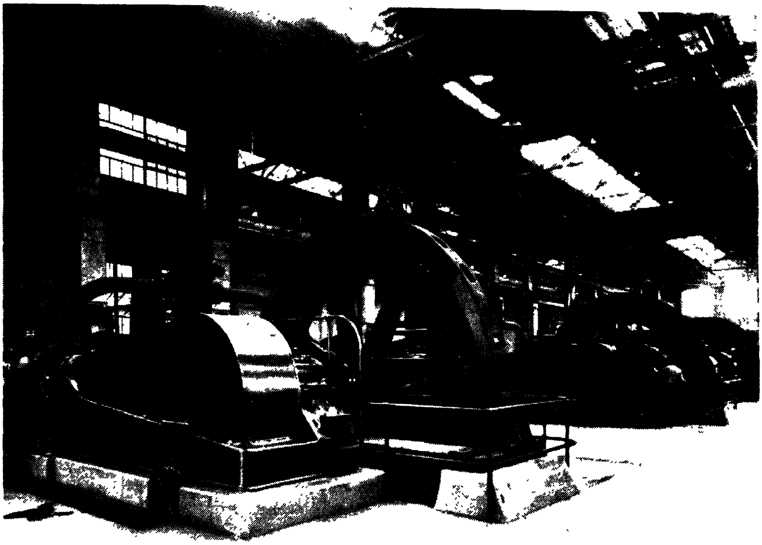


FIG. 257.—Du Pont de Nemours synthetic ammonia plant.

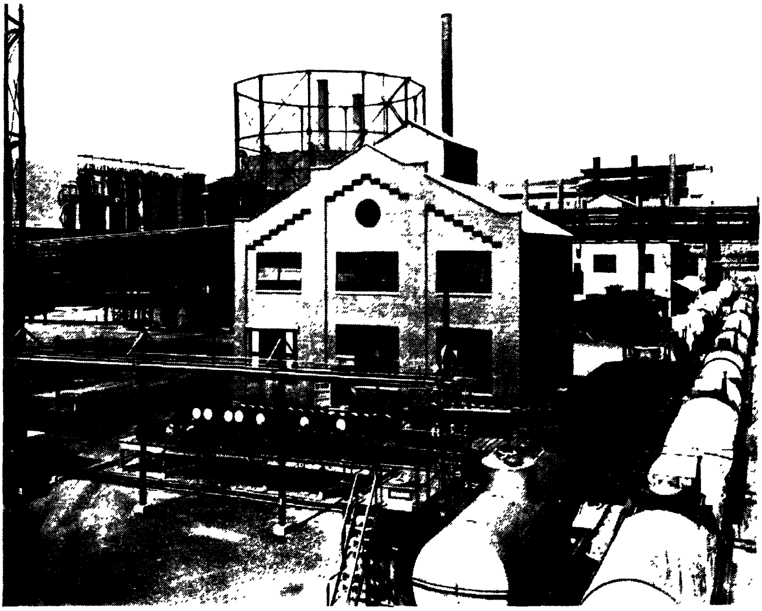


FIG. 258.—General view of water-gas plant. Du Pont de Nemours synthetic ammonia plant.

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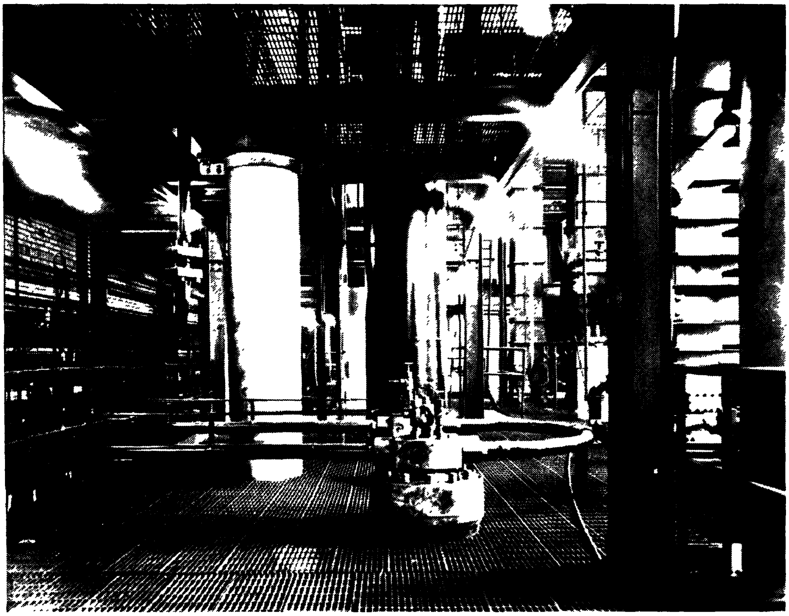

FIG. 259.—Du Pont de Nemours synthetic ammonia plant. View inside catalyst tube room.

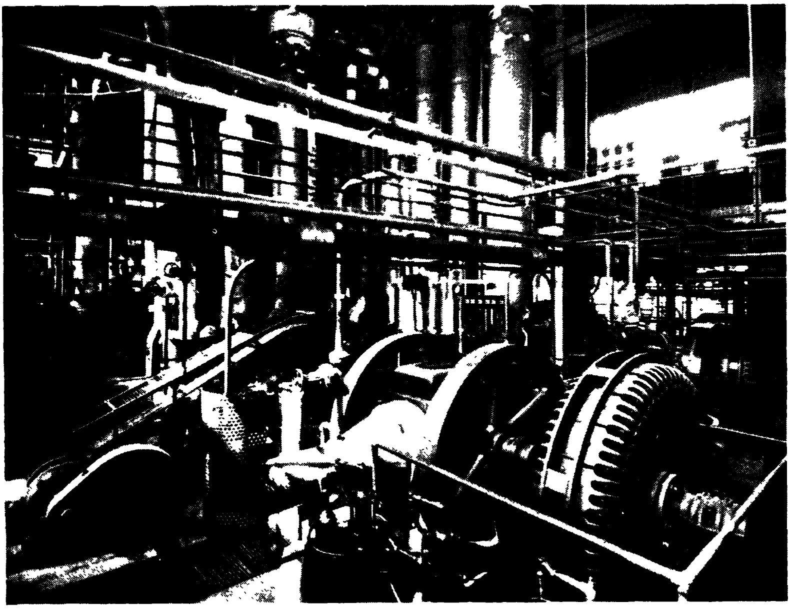

FIG. 260.—Du Pont de Nemours high-pressure research laboratories.

[*See page* **376.**

considerable interest. I am indebted to the Du Pont Co. for permission to publish it :—

"E. I. du Pont de Nemours & Co.,
" *Wilmington, Del., May 8, 1933.*

"Hon. George W. Norris,
"*Senator from Nebraska, Washington, D.C.*

" Dear Senator Norris,

" I read your address of May 1 on Muscle Shoals and your presentation of the bill you propose in the Senate with much interest and appreciation. May I congratulate you on your position in the matter, which seems to me both courageous and full of wisdom.

" Because of our large investment in the fixation of atmospheric nitrogen in the manufacture and sale of nitrogenous products we have felt that we might be misunderstood and criticised if we took any part in the long controversy regarding the disposal of Muscle Shoals. We have, therefore, scrupulously refrained from any approach on the matter to members of this Congress or its predecessors. Indeed, I am quite sure that the only contact which any Du Pont man in a position of authority has had with a Member of Congress was our invitation to you to visit our plant at Belle, W. Va. May I add that my own recollection about that visit was not that you wrote us requesting permission to see the plant, but rather that, understanding that you might be interested in such a visit, I promptly called you up and told you how glad we would be to have you see what we were doing. That spirit of co-operation still exists, and if there is any information that we can contribute which would be helpful to your handling of the nitrogen phase of the Muscle Shoals matter we shall be very glad to respond, consistent, however, with our unwillingness to take up any controversial position.

" You described synthetic ammonia as being the Haber process. It is probably not important but may be interesting to you that the Du Pont Co. did not follow the Haber process, but acquired rights to a French process and an Italian process for the synthesis of ammonia, adapted the best features of these to American conditions, and made ourselves noteworthy contributions to the art, so that our present process is distinctively our own and is not derived from the Haber process. It is true that the Haber-Bosch process was the first successful commercial synthesis of ammonia, worthy of great credit in this scientific development, but our work in this country has not been one of imitation. We are proud of our plant at Belle, of its efficient performance, amazingly low cost of production, and its large potential capacity, though unfortunately its capacity is only being partly utilised on account of what has been in reality dumping at prices far below the cost of production, of enormous quantities of nitrogen products imported into this country from Europe and Japan over the past three years.

"Incidentally, as you yourself pointed out, American nitrogen plants now have ample capacity to supply all American nitrogen requirements. Even record-breaking demands for fertiliser nitrogen would not occupy them all fully. Prices in this country are the lowest in the world, except the fictitious or rigged prices in Holland, and they are the lowest prices for nitrogen compounds in history. Increased production in our plants to supply all American needs would give employment to hundreds more of American workmen in these factories and in the coal mines, were it not for this organized foreign attack on our market with which we have had to contend.

"In your speech you made the excellent and very true point of the decreased consumption of power in the cyanamide process compared with the arc process, and above all, in the synthetic ammonia process compared with cyanamide. The arc process is obsolete and abandoned, cyanamide is on the decline except for special uses. But I did not notice that you pointed out that the reason for locating our plant in West Virginia was not the abundance of high-quality coal for producing power, for the power requirements in synthetic ammonia are relatively low, but rather the abundance of good coal for the production of coke as the raw material for making hydrogen. After all, that is the gist of the matter. Though called the fixation of nitrogen, nitrogen is presented to us almost without cost by the atmosphere, and that exists everywhere. The expensive ingredient in making ammonia is hydrogen, and it seems quite certain that hydrogen derived from any gas at real market value or produced by the electrolysis of water with electric power at any equitable price cannot economically compete with hydrogen made from coke produced from good-quality, low-cost coal. That is the reason, therefore, to make cheap hydrogen, that we located our ammonia plant in a good coal region.

"I trust that these comments may be of interest to you and perhaps of some use in any further statements you may have occasion to make in addition to your speech of May 1, which dealt so excellently with the questions at issue.

"With kind personal regards,
"I am, yours sincerely,
"JASPER E. CRANE."

Three illustrations of the synthetic ammonia plant of Imperial Chemical Industries at Billingham are given in Figs. 261, 262, 263.

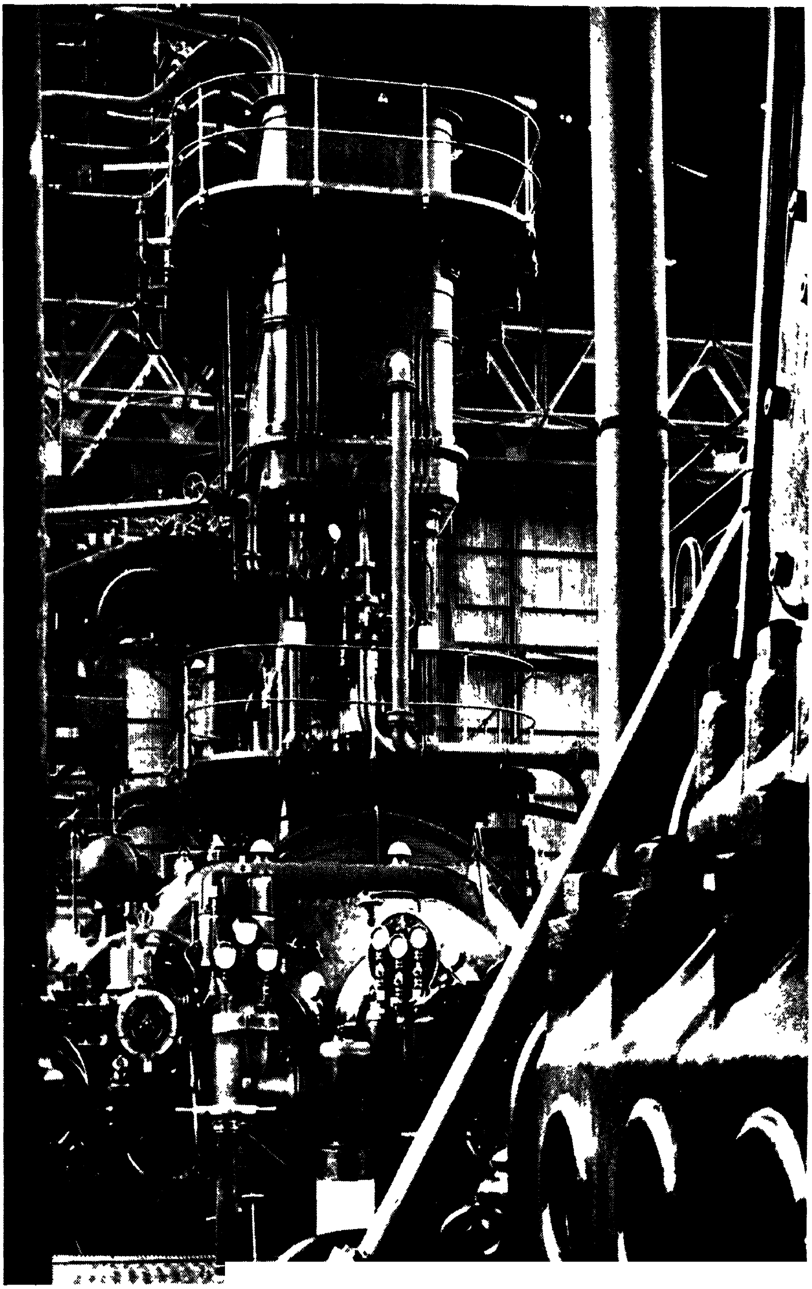

FIG. 261.—Large hydrogen-nitrogen compressors at Billingham. (Imperial Chemical Industries Ltd.)

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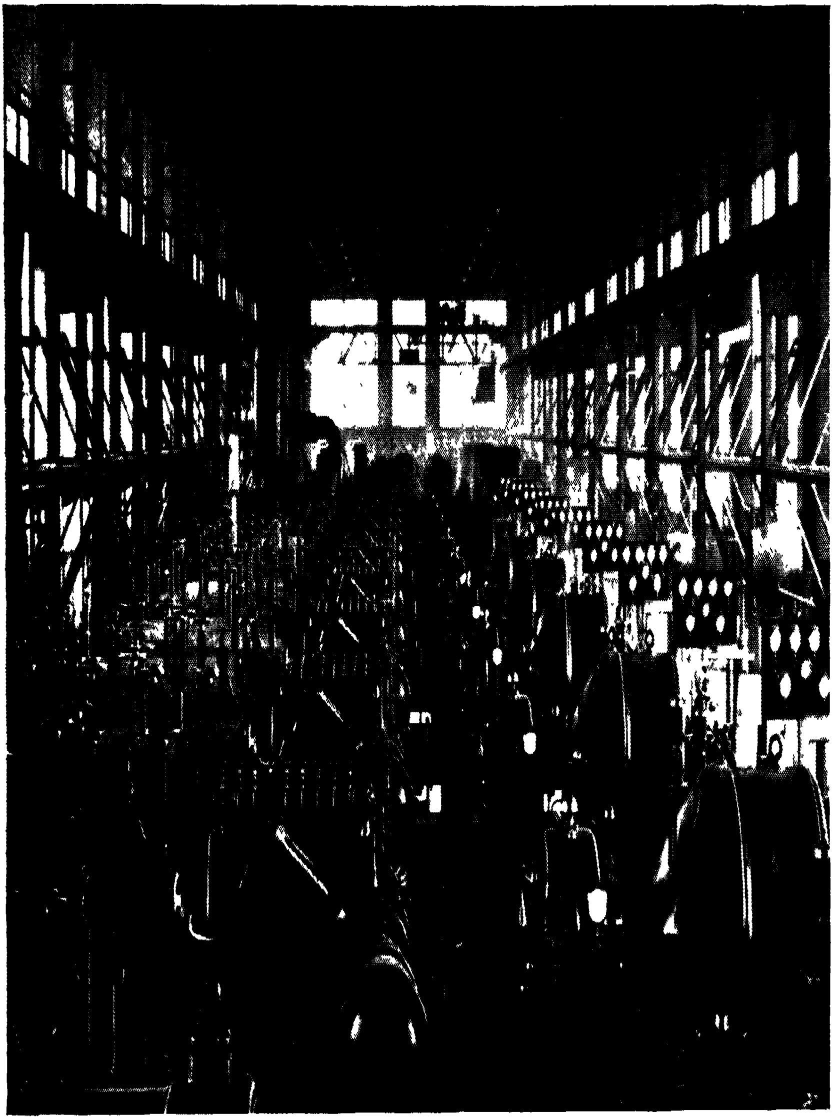

FIG. 262.—High-pressure liquor pumps at Billingham. (Imperial Chemical Industries Ltd.)

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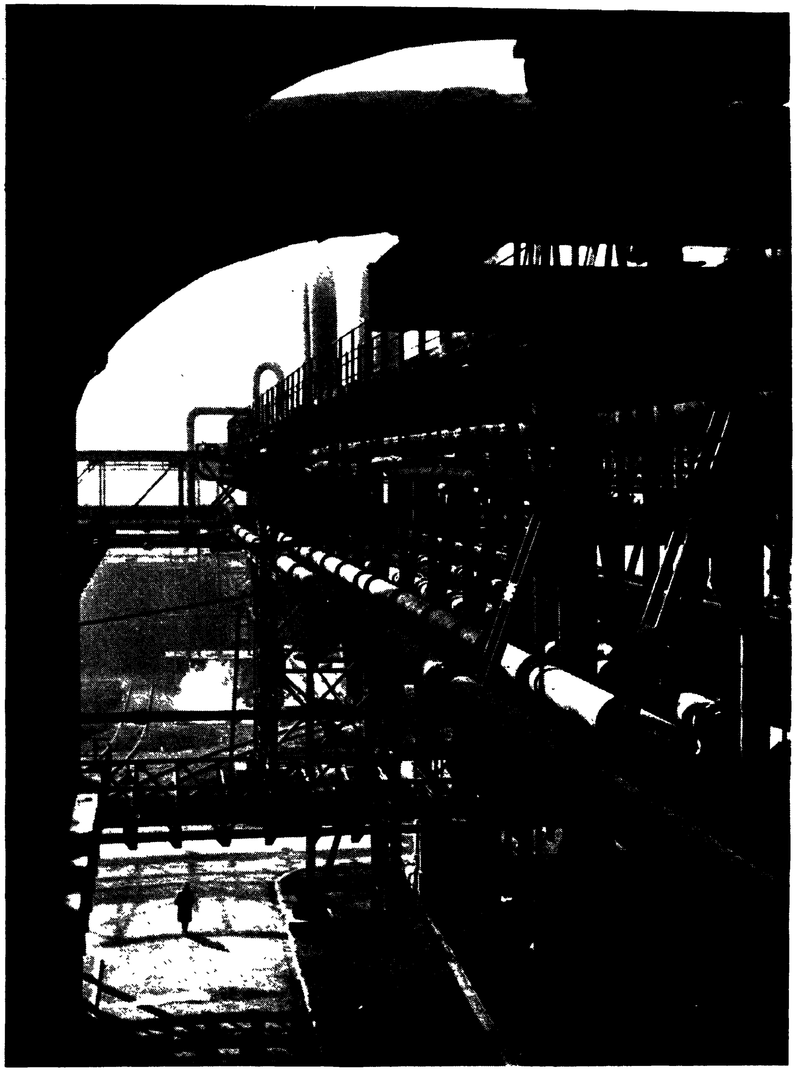

FIG. 263.—View showing massive pipe bridges at Billingham. (Imperial Chemical Industries Ltd.)

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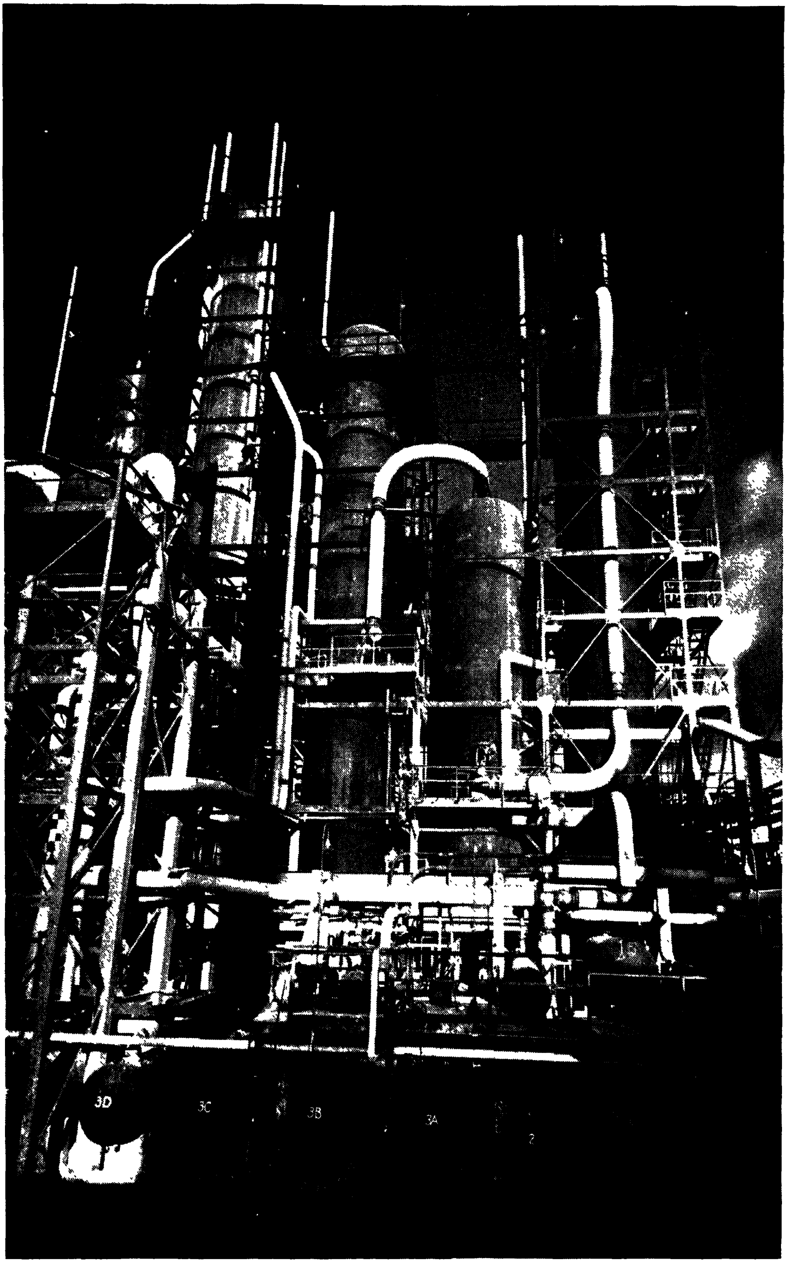

FIG. 265.—Standard Oil Co. of Indiana. Whiting refinery. Combined crude topping, viscosity breaking, vapour-phase cracking, naphtha reforming and gasoline stabilising unit.

[*See page* 384.

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Fig. 261 shows one of the large hydrogen-nitrogen gas compressors, Fig. 262 shows an installation of high-pressure liquor pumps, and Fig. 263 an example of the pipe bridges typical of the Billingham works.

As mentioned in Chapter I., these works have a capacity of 200,000 tons of fixed nitrogen per year, and is now the scene of considerable activity during the erection of the first large plant for the hydrogenation of British coal to produce motor spirit and oils.

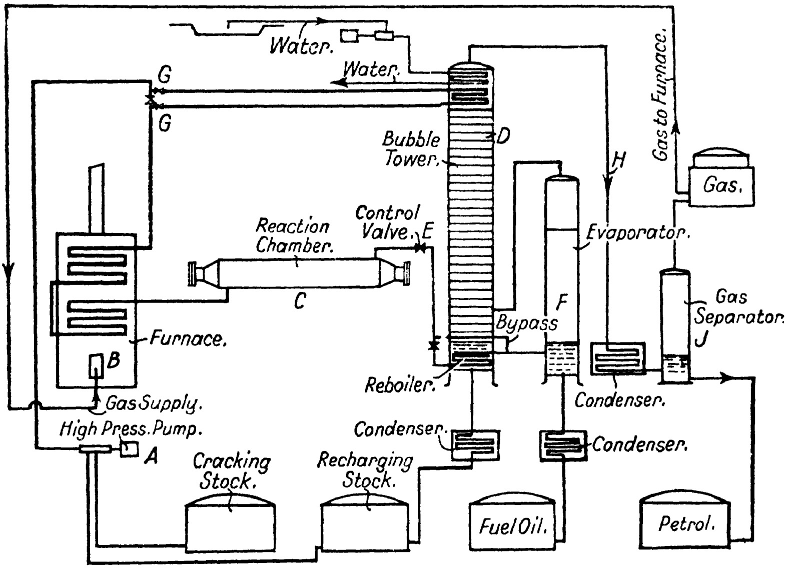

FIG. 264.—Layout of " Cross " cracking plant.

In Chapter I. it was stated that pressure is being increasingly applied to the " cracking " of petroleum fractions to produce light motor spirit, and the flow sheet (Fig. 264) shows the layout of a " Cross " cracking plant (*Trans. Inst. Chem. Eng.*, 1927, **5**, 89). The pump " A " delivers the oil to the pipe still or oil-heating furnace " B," either direct or through the preheating coils at the top of the dephlegmator " D." In practice, the oil leaves the furnace tubes " B " at a temperature of 850-900° F., and the average rate is 3 ft. per sec., and incipient cracking takes place in the lower bank of the tubes. The heated oil then passes to the reaction chamber " C," and this is a very essential feature, as it creates the necessary " time lag " required for oil cracking. It consists of a single hollow forging, 42 ft. 6 ins. long and 3 ft. 2 ins. internal diameter, with 4-in. thick walls. This reaction chamber is heavily lagged to prevent heat losses, and the oil within it is maintained at a pressure high enough to ensure that the heated oil is in the liquid phase, viz. 750 lbs. per sq. in. In this chamber " C," and remote from the point of oil entry, a regulating valve " E " is fitted, and this controls the rate of flow of the oil through the plant.

The vapour line beyond the control valve " E " allows the gas to pass into the vaporiser " F," but before reaching " F " the vapour line has a by-pass, which when opened allows the vapours to pass through a reboiler situated at the base of the dephlegmator. Here the temperature of the oil gases or vapours which left the reaction chamber at 750° F. give up part of their heat in re-evaporating the light boiling fractions that are meshed in the heavy ends called recharging stock, which have been condensed, and have fallen to the base of the dephlegmator " D." The reheating of this stock causes a continuous stream of revaporised oil to issue from the condensate and ascend the trays in the dephlegmator, the oil in the base of which is maintained by this heat exchange at a temperature of 650° F. The vapour from the reboiler passes into the evaporator " F," which is a cylindrical chamber built to withstand a working pressure of 70 lbs. per sq. in., but which is normally at a working pressure of 15 lbs. per sq. in. The top of the evaporator is provided with a plate packing as shown. This packing provides resistance to the passage of the vapours which in escaping and expanding are cooled, and reject the immediately condensing heavy ends. The latter constitute a stock too unresponsive to recrack, and this is used as fuel oil. The remaining vapours are led to the " bubble tower " dephlegmator, where the ascending gases meet a descending stream of condensed oil, and finally a water-cooling coil, and the cold charging oil coils disposed at the top are shown.

The temperature of the vapour leaving the dephlegmator is about 260° F., and the vapour line " H " conveys the vapours to the condenser and the gas separator " J." Here the crude petrol is separated from the fixed gases which escape to a gasholder and which may be scrubbed if desired to recover the more volatile constituents. The gas separator " J " is fitted with an automatic regulator, which allows the escape of the crude petrol which is drawn off and delivered to the crude petrol tank, through which it passes to the refinery.

COMBINED CRUDE TOPPING, VISCOSITY BREAKING, VAPOUR-PHASE CRACKING, NAPHTHA REFORMING AND GASOLINE STABILISING UNIT FOR STANDARD OIL COMPANY (INDIANA), WHITING, INDIANA.

The M. W. Kellogg Co. have recently completed and put into operation what is probably the most interesting refining unit now in operation in any oil refinery.

The economic conditions in the oil-refining industry, during the past few years, have demanded that oil refining be placed on a strictly manufacturing basis, and the present plant was designed to produce gasoline suitable for the present-day market, at the minimum unit cost.

It was designed and built for the Standard Oil Company (Indiana) to process 19,000 barrels (42's) of Mid-Continent crude, and to produce therefrom a stabilised gasoline of a high iso-octane number.

This unit has now been in operation for more than six months. processing 20,000 barrels (42's) per stream day of 36-37° A.P.I. Mid-Continent pipe-line crude, and producing therefrom 70 per cent. of stabilised gasoline having an octane number of 70 and showing approximately 18 per cent. off at 158° F. by the A.S.T.M. distillate method.

The fuel oil has a flash of over 300° F. and a viscosity of below 200 sec. Saybolt Furol.

Description.

The operations of crude topping, naphtha reforming, viscosity breaking and vapour-phase cracking, together with gasoline stabilising, have been combined in this plant so that all operations are carried on simultaneously.

While all operations are carried on concurrently, the unit is sufficiently flexible so that every operation can be independently controlled and conducted under the most suitable conditions of temperature and pressure to achieve the desired result.

The topping operation, which is accomplished entirely by waste heat, removes a light fraction of straight run gasoline, a heavy naphtha fraction, and a light gas oil fraction.

The light straight run gasoline has a gravity of approximately 70° A.P.I. and an end-point from 300 to 325° F.

The naphtha fraction is charged directly to the reforming coil in the vapour-phase furnace.

The light gas oil fraction is pumped to the high-pressure fractionating system where it eventually forms part of the charging stock to the vapour-phase furnace.

The topped crude passes to the upper section of the fuel oil flash tower, where it combines with the heavier cycle stock. The combined feed is then pumped to the high-pressure evaporator for additional direct heat exchange and then flows to the viscosity breaker accumulator, from which it is pumped to the viscosity breaking furnace. This furnace is operated so as to produce some cracked gasoline and a suitable charging stock for the vapour-phase portion of the unit.

The vapour-phase charging stock is fractionated out in the high-pressure bubble tower and accumulates in the bottom section, from which it is drawn by means of a hot oil pump and circulated through the vapour-phase furnace. The lighter ends are removed from this stock by stripping with water.

The fuel oil formed from the primary and secondary cracking operations accumulates in the bottom of the high-pressure evaporator, from which it is drawn to the combination fuel oil flash and the crude topping tower operated at low pressure. Here the fuel oil is flashed to the desired gravity and viscosity before passing from the system.

The flash distillate from the fuel oil passes to the second section of the fuel oil flash tower, where direct heat exchange takes place with the topped crude, the heavy distillate condensed, and carried along with the topped crude, while the light distillate suitable for vapour-phase charge stock passes overhead to the third section of this tower, from whence it is returned to the high-pressure fractionatting system together with the virgin light gas oil fraction of the crude previously mentioned.

All of the cracked gasoline and gas from the three operations of naphtha reforming, viscosity breaking, and vapour-phase cracking passes from the top of the high-pressure bubble tower to the high-pressure gas separator. This separator is so operated as to release a dry gas from the top of a low butane and heavier content.

The raw gasoline is pumped from the bottom to a high-pressure stabiliser. Here the remaining fixed gases are released and a stabilised gasoline of the desired vapour pressure is drawn from the bottom.

Operating Characteristics.

This unit is extremely stable and steady in operation, and under the operating conditions outlined above will remain on stream 25 days.

The fixed gas is low for the character of the gasoline produced, being approximately 700 cu. ft. per barrel of cracked gasoline.

The fuel consumption is approximately 5½ per cent. based on the crude charge.

Only four men are required per shift to operate the entire plant, although five are being used at the present time because it is comparatively a new unit.

Typical distillation of the feed and products are as follows :—

	Crude Feed.	S.R. Gasoline.	Stabilised Cracked Gasoline.	Blend of S.R. and Cracked.	Residue.
Gravity A.P.I.	37·0°	70·4°	58·6°	61·2°	8·0°
I.B.P.	140° F.	83° F.	93° F.	84° F.	—
10 per cent.	226	127	130	126	—
20 " "	310	154	164	160	—
30 " "	392	175	200	192	—
40 " "	474	195	234	221	—
50 " "	559	210	261	245	—
60 " "	650	224	287	270	—
70 " "	—	239	314	300	—
80 " "	—	261	341	334	—
90 " "	—	296	374	374	—
E.P.	—	318	406	403	—
Per cent. over at 158° F.	—	28 %	22 %	23·5 %	—
Octane number	—	59·5	72·0	70·0	—
Flash	—	—	—	—	315° F.
Viscosity S.F. at 122° F.	—	—	—	—	187″

Mechanical Construction.

The viscosity breaking furnace is entirely steel encased and is designed for a heat release of 71,000,000 B.Th.U. per hour.

The vapour-phase and naphtha reforming furnace has two independent radiant sections with a common convection section. This furnace is also entirely steel encased, and is designed for a total heat release of 216,000,000 B.Th.U. per hour.

The main tower system of the cracking unit operates at a pressure of 250-200 lbs. while the stabiliser operates at the higher pressure of of 450-350 lbs.

All these large towers, which weigh from 280,000 to 300,000 lbs. each, together with the various smaller towers and accumulators, are of Kellogg master-welded construction and were manufactured in the plant of the company at Jersey City, N.J. These towers are all built to conform with Class 1 specifications, which include the X-raying of all seams, and are designed with sufficient corrosion allowance to provide a life of ten years. (Details of these large pressure vessels are given in Chapter X.).

The viscosity breaking charge pump has a capacity of 30,000 barrels per day, and the vapour-phase charge pump has a capacity of 40,000 barrels per day, based on cold volume.

The quantity of 240,000 barrels of oil per day is pumped to this unit in the various stages of processing. With the exception of one or two smaller pumps, all this oil is handled by means of centrifugal pumps. Most of the oil in process is pumped at a temperature of more than 500°, and the volume handled by each of these pumps on a hot oil basis varies from 30,000 to 55,000 barrels per day. If reciprocating pumps had been used in the design of this plant, the pump house alone would have occupied more than three times its present ground space.

The operation of this unit has been so satisfactory in all respects that a second unit is now in process of construction, which will charge 32,000 barrels of East Texas crude per day and produce gasoline, kerosine, low cold test furnace oil and Bunker C fuel oil as products. In this new unit vapour-phase clay treatment of the gasoline will be used, therefore the final product gasoline is substantially finished and ready for use.

This extract is taken from the paper by J. V. Jirasek, which was read before the recent World Petroleum Congress, London (July, 1933). I am indebted to the Standard Oil Company of Indiana for the very impressive photograph of this unit (Fig. 265). The furnaces are just off the edge of the picture to the right ; reading from right to left the various towers are respectively the reaction chamber, the evaporator or tar separator, the bubble tower for cracked products, and the crude oil flash and bubble tower and lastly the gasoline stabilising tower.

Details of the dimensions and construction of the various vessels of this unit are given in Chap. X.

Polymerisation and Partial Oxidation of Olefines, etc., under Pressure to produce Liquid Fuels.

Attention has been turned in recent years to various possible means of utilising the gaseous olefines present in certain industrial gases. For example, gases produced simultaneously with petrol in oil-cracking operations constitute a rich source of these olefines. especially in the case of the vapour-phase (or high temperature-low pressure) cracking processes. The gases produced in coal carbonisation also contain olefines.

A recent paper by Bowen and Nash (*Proc. World Petroleum Congress*, London, 1933) deals with the formation of liquid fuels by polymerisation of these olefines, which have a marked tendency to polymerise under influences such as ultra-violet light, silent electric discharge, heat, pressure, catalysis or combinations of these.

From free energy calculations it has been shown that olefine hydrocarbons tend to polymerise below about 425° C., above which temperature cracking takes place, whilst the isomerisation of the higher olefines into the corresponding naphthenes is possible below that temperature. The polymerisation processes are usually exothermic and are favoured by low temperatures and hence catalysts.

In general, at lower temperatures the polymerisation products of olefines include higher olefines and naphthenes, at medium temperatures higher olefines, paraffins, naphthenes and poly-naphthenes, and at higher temperatures secondary reactions cause the formation of aromatic hydrocarbons.

Research upon the formation of liquid fuels by polymerisation of gaseous olefines can be divided under three headings :—

(1) Polymerisation under pressure and at moderate temperatures ;

(2) Polymerisation under atmospheric pressure at high temperatures ;

(3) Polymerisation under pressure in the presence of anhydrous aluminium chloride.

The conversion of gaseous olefines into liquid polymers at moderate temperatures and under pressure, without catalysts, is nearly complete, and a high proportion of the crude oil boils in the spirit range. The liquids formed under these conditions are not aromatic and they contain paraffins, naphthenes and higher olefines, such as the hexenes, in considerable quantity. The spirit produced under these conditions is about five-sixths as good as benzene in anti-knock value when rated on a volume basis.

At high temperatures, in the absence of catalysts, gaseous olefines are readily converted into aromatic hydrocarbons with quite good yields. The liquid products are similar to those obtained in the pyrolysis of paraffin gases at high temperatures, but the temperature necessary for the conversion to aromatic liquids is lower in the case of the olefine than the paraffin gases. The spirit fraction, containing benzene and other aromatic hydrocarbons, including toluene, would thus be of good anti-knock value.

In the case of the polymerisation of olefines with aluminium chloride, ethylene has received the most attention. This gas polymerises under suitable conditions to a crude oil about half of which is spirit. This spirit is practically wholly paraffinic and has an octane number of between 70 and 80, the hydrocarbon constituents being, probably, to a large extent of the branched-chain type. This spirit has a very low freezing-point. Undoubtedly the immediate homologues of ethylene would give very similar results.

A paper by Newitt and Townend read before the same congress also deals with the utilisation of natural and cracked gases. The authors of this paper are of the opinion that the most direct method of obtaining oxygenated liquid products from the paraffins and olefines is by their partial oxidation, and the following is a summary of their paper, which describes apparatus and methods whereby these gases may be oxidised under conditions of temperature and pressure such that large yields of alcohols, aldehydes and acids are obtained.

Thus, for example, in the case of methane, by employing a pressure of 106·4 atmospheres and a temperature of 341° C., 22·3 per cent. of the methane burnt appears in the products as nearly pure methyl alcohol.

For ethane the results are still more promising. The liquid products of its pressure oxidation are ethyl and methyl alcohols, acetaldehyde and acetic acid together with water and traces of formaldehyde and formic acid. In one experiment at 100 atmospheres and 272° C., 71·7 per cent. of the carbon of the ethane burnt was found in the condensed products, which had the following composition :—

	Per cent.
Ethyl alcohol	51·0
Methyl alcohol	28·0
Acetaldehyde	11·1
Acetic acid	9·0
Formaldehyde	0·3
Formic acid	0·6
	100·0

Other methods of obtaining oxygenated products, such for example as the hydration of olefines, were briefly reviewed and discussed.

Continuous Hydrogenation of Liquid Oils to Produce Fats.

The hydrogenation of liquid oils to produce solid fats is another instance of a chemical change which is facilitated by pressure, and, as will be seen, it is suitable for operation as a continuous process.

Solid fats are of economic value in the manufacture of edible products such as margarine and lard substitutes, and non-edible products such as soap and candles, the quantities required for these purposes being, in the aggregate, much greater than those of the liquid fats or fatty oils, whose main outlets, in addition to soap, are for paints, lubricants, burning oils, leather dressing, etc. Liquid fats, however, preponderate in nature over those which are solid at ordinary temperature, and the latter accordingly tend to be more valuable and possess a higher market value.

One of the largest constituents of the liquid oils used for fat-hardening is olein, the glyceride of oleic acid, which is converted into a solid product stearin, the glyceride of stearic acid. Reference to the formulæ of these two (oleic acid—$C_{18}H_{34}O_2$; stearic acid—$C_{18}H_{36}O_2$) shows the change which takes place in the actual process. The difference between the two substances is simply that stearic acid contains two more atoms of hydrogen than oleic acid ; hence the object of the whole process is to add the two atoms necessary to accomplish the transformation.

Although olein is the main constituent of most natural oils, the products of animal and vegetable origin are really very complex mixtures, and contain, in addition to olein, numerous other glycerides, related to it in chemical constitution, some of which require more than two atoms of hydrogen for conversion into stearin.

Attempts were made for many years to find a means of carrying out what is now so easily accomplished by the hardening process, using nickel as a catalyst, for it has long been evident that oleic acid and its glyceride olein occur abundantly in liquid oils such as cotton, linseed, soya bean, rape, whale, herring, seal oil, etc., while there was a definite shortage of the solid fat stearin, the basis of nearly every edible and non-edible fat.

In the course of his classic work on the catalytic hydrogenation of the vapours of organic compounds in the presence of nickel, Sabatier observed that oleic acid was thus transformed into stearic acid, but he believed that hydrogenation only occurred in the state of vapour. In 1902, however, Normann found that reduced nickel oxide when suspended in fatty acids or fatty oils in the presence of hydrogen, effected hydrogenation in the liquid state. This discovery, which may be looked upon as the foundation of technical fat-hardening, was developed in the course of the next decade into a process suitable for large-scale working, and by about 1910 the output of hydrogenated fats probably amounted to several hundred tons per week. The war gave an immense stimulus to the industry, for without it a serious shortage of soap, candles, margarine and lard substitutes would no doubt have resulted ; capacity was rapidly extended and in 1918, the world's potential output of hardened fats had reached many thousands of tons per week. Since that time the demand for hardened fat has somewhat declined, but the industry is nevertheless firmly established on a large scale ; it helps to keep a balance between the costs of soft and hard fats, while as the prejudices against hardened products have died away, it is very probable that the use of hydrogenated fats will increase rather than diminish.

Were it not for the discovery and commercial application of hydrogenation, the great whale oil industry, with its immense floating factories, could not have reached its present magnitude. By no other known commercial process can the fishy smell be removed so as to render the oil suitable for soap and edible purposes.

The original process of hydrogenation devised by Normann, together with important later modifications, has now merged into the general title of "powder process," in which the catalyst is prepared by reducing nickel carbonate in hydrogen at a temperature of 300-350° C., the pyrophoric powder so obtained being added to the oil to be hydrogenated.

Modern methods may be divided into (1) batch processes and (2) continuous process, although in some cases there is no clear line of demarcation between the two.

In the majority of batch processes the use of powder catalysts, with or without supports, is involved, and in such cases the rapidity and economy of the process depends upon the degree of contact of the phases involved, namely: a gas (hydrogen), a liquid (oil), and a solid (catalyst). Various inventions have been recorded in order to increase such contact; these may be classified broadly into (1) agitation systems, in which mechanical agitation is used to produce an intimate mixing of the nickel, fatty acid and hydrogen, and (2) circulation processes, in which a mixture of oil and catalyst is withdrawn from the lower part of the reaction vessel, and injected under pressure as a fine spray into the gas-space at the top of the vessel.

The continuous process was developed considerably later than the others, and appears to offer several advantages over the earlier methods, since it has been proved that the preparation, regeneration, and efficiency of the stationary catalyst are technically satisfactory. The following brief description relates to the continuous process of Technical Research Works Ltd., developed by Bolton and Lush, which introduces an entirely novel principle in the reactivation by anodic oxidation of the spent catalyst. The catalyst used in the process is in compact form and consists of a mass of oxidised nickel turnings, wool or wire contained in an openwork nickel frame, as shown in the illustration, Fig. 266. The surface of the nickel is rendered catalytic, either by immersing it as the anode in a dilute solution of sodium carbonate which is electrolysed at a suitable current density, or by steeping it in a bath of dilute sodium hypochlorite of definite concentration. The metal thus receives by either process, a superficial coating of an adherent film of oxide which yields an active catalyst when, after washing and drying, it is replaced in the hydrogenation tubes and exposed to the action of hydrogen at about 250-300° C.

A stream of oil and hydrogen is passed over the catalyst contained in a number of tubes in series, and the hydrogenated oil thus produced leaves the plant in a clear and bright condition requiring no filtration. The time of contact of the oil with the nickel catalyst is only a very few minutes which is stated to be an advantage over the "powder" process in which the contact is considerably pro-

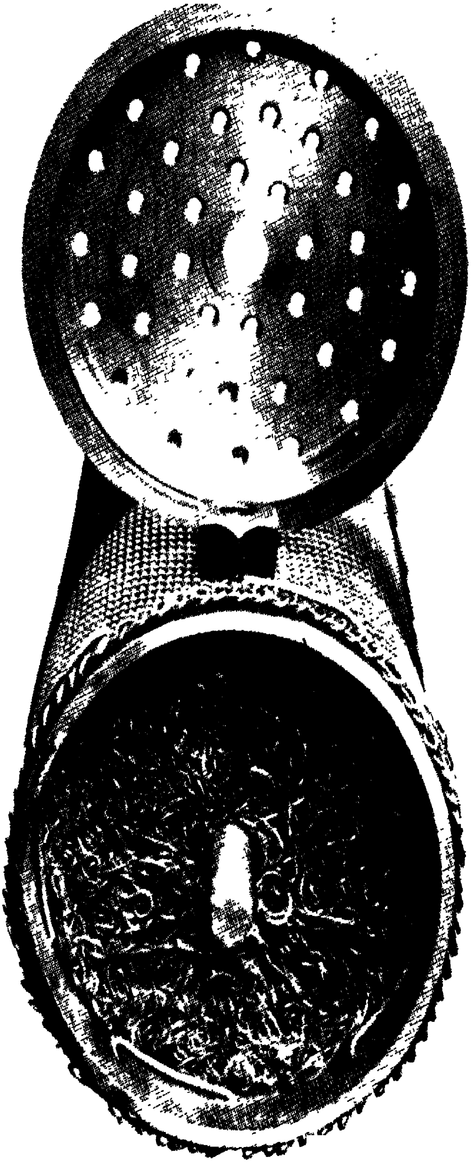

FIG. 266.—Technical Research Works, Ltd. Continuous hydrogenation plant. End view of catalyst frame.

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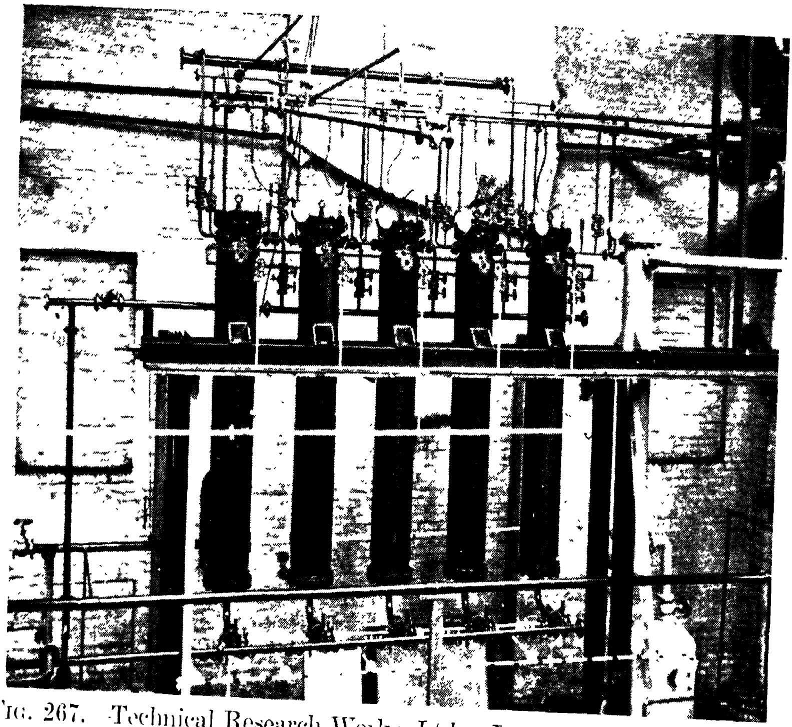

FIG. 267. Technical Research Works, Ltd. Large-scale hydrogenation plant.

FIG. 268.—Technical Research Works, Ltd. Continuous hydrogenation plant. View of catalyst frame.

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longed. The control of the process is simple and any desired degree of hydrogenation of the oil can be obtained by adjusting the rate of flow of the oil through the plant.

It is claimed that a unit hardening only 5 tons of oil a week will pay, but the process is in commercial operation in much larger units than this, standard units of 100 tons per week being in use, and multiples of these are manageable at a low increase of overhead charges.

The photograph, Fig. 267, shows a works-scale plant, built by Technical Research Works Ltd. The large vessel on the right is the reservoir for the oil to be treated, the oil being forced by hydrogen pressure through the exit on top. After passing through a sight gauge, it is met by a stream of hydrogen which mingles with it in its passage up and down through the four vertical reaction vessels and thence into a separator on the left, from which the hydrogenated oil passes, by gravity, to a cooling coil, and is collected ready for use. The hydrogen is returned into the system from the separator, through a trap, by means of a pump.

One of the cartridge-like cages which contain the nickel catalyst may be seen in front of the apparatus (see also the illustration, Fig. 268).

The large factory models, being similar in design, are of equal simplicity, and require the minimum of attention once the continuous flow has been set.

The advantages claimed for this process are as follows :—

(1) Continuous operation.

(2) The hydrogenated oil flows from the apparatus in a clear and bright condition, and needs no filtration.

(3) The catalyst may be regarded as part of the plant, and can be revivified by anodic oxidation and subsequent reduction, for years without appreciable loss.

(4) Control of composition of the hydrogenated product (selection).

(5) The output of the plant is inversely proportional to the extent of hydrogenation.

(6) There is no "splitting" of the oil, with formation of free fatty acids ; consequently subsequent neutralisation by alkali is not necessary.

(7) The oil is heated for about 10-15 minutes only during the operation of hydrogenation.

(8) Low cost of operation.

An average figure for hydrogen consumption over the range of oils dealt with in a fat-hardening installation is about 1 per cent. by weight of the fatty oil treated, or about 3000 cubic ft. of hydrogen per ton of oil, but the actual amount of hydrogen with which different fats combine is, of course, dependent on their original state of unsaturation and on whether they are to be converted into hard tallow-like fat, soft fat, or semi-liquid fatty oils.

The continuous process of Technical Research Works Ltd. is suitable for the hydrogenation of chemicals, some of which are dangerous to handle, such as phenol; others require strict temperature control such as aldehydes; while others are sensitive to unreduced nickel oxide, such as furfural. Phenol, cresol, naphthalene, pyridine and crotonaldehyde are being hydrogenated on a commercial scale.

CHAPTER X.

CONSTRUCTION AND MANUFACTURE OF LARGE PRESSURE VESSELS FOR HIGH-TEMPERATURE SERVICE.

For working pressures over 450 lbs./sq. in. or so, riveted construction of large pressure vessels is in many instances unsatisfactory, and a process known as "hollow forging" has been developed for such cases. This process consists briefly in manufacturing the pressure vessel from a solid ingot by piercing to remove the core and subsequent forging to the required form.

The forms adopted by designers of pressure vessels vary greatly: in some cases large diameter and small length is required: in others long length and very small diameter. In most cases of large vessels the dimensions are governed by considerations of maximum weight of the hollow forgings which the steel-maker is able to produce.

In general, the requirements of the designers of such vessels have necessitated the production of tubes of diameters between 3 ft. and 5 ft., and of lengths up to 50 ft. For the largest vessels ingots weighing as much as 175 tons have been used, and even larger ingots are now under consideration. Such an ingot as produced by the English Steel Corporation is shown in Fig. 269. It was cast from three Siemens open hearth furnaces, and is for one of the boiler drums of the Stirling boiler plant for the Fulham Power Station, which is now under construction.

The following are the sizes of the finished drums for this station:

	Length.	*Internal Diameter.*	*Wall Thickness.*
Front steam drums .	39′ 8½″	3′ 6″	3⅛″
Rear steam drums .	40′ 9½″	4′ 6″	4⅜″
Mud drums . .	37′ 0½″	4′ 6″	3⅞″

The boilers are to operate at a steam pressure of 625 lbs./sq. in., with a total temperature of 850° F. Naturally the operating temperature of these drums corresponds to the temperature of saturated steam at 625 lbs. sq./in. pressure, i.e. considerably less than 850° F., which is the temperature of the steam leaving the superheater.

In producing hollow forgings, the practice of most steel-makers is to anneal the ingot after stripping it from the mould (whilst still hot), and afterwards allowing it to cool very slowly. When cooled, a hole is trepanned through the centre, and Fig. 270 shows a trepanned ingot at the works of Thos. Firth & John Brown, Ltd. The object of this operation is, firstly, to produce a core of metal which can be then closely examined, and, secondly, to remove the less pure material from the axis of the ingot. Fig. 271 shows the trepanning operation being carried out at the Vickers Works of the English Steel Corporation Ltd.

It will be realised that the cooling of an ingot weighing 100 tons or more may occupy a period of three to four weeks, and in order to obviate this, and the stresses caused by cooling, the English Steel Corporation has developed a process of hot piercing or punching, whereby a hole is made through the ingot without cooling it. In this process, the feeder head at the top and the surplus metal at the bottom of an ingot is cut away by means of a large cutter or knife, which is driven through the ingot by means of an hydraulic press. The remaining body of the ingot is next placed under a press, so that its axis is vertical, and a tubular punch is driven axially through the ingot. By this means, a central core is removed, which, of course, contains the less pure material from the axis of the ingot, and a hollow billet is thus prepared from which the forging is made by the usual processes ; this is common to both the hollow billets prepared by the hot process just described, or the annealing and slow cooling process with subsequent trepanning of the core.

The first operation (after reheating in the latter case to the requisite temperature) is to enlarge the hole by an hydraulic pressing operation ; the top tool of the press presses the wall of the hollow billet against a bar which passes through the hole and is independently supported at each end (see Fig. 272).

The long tubular forging is produced by successive heats or forging operations, between each of which the forging is reheated. The middle of the tube is forged first. After the middle is finished, one end is recharged and the other end, still in the rough state, is usually left outside the furnace.

In Fig. 273 the middle and one end of the tube have been forged, and for this large drum eight or more " heats " are required to complete the forging operation. Fig. 274 shows this tube completely forged. It is 44 ft. long, and weighs 100 tons. It was one of a set of thirty-two such drums supplied by the English Steel Corporation for the power station of the Imperial Chemical Industries Ltd., at Billingham. After forging, such drums are normalised, the outside is rough machined, and the interior is then bored. After reheating the ends are closed in for manhole openings, and the complete drum with holes drilled for the water tubes is shown in Fig. 275. It is for a boiler with a working pressure of 800 lbs. per

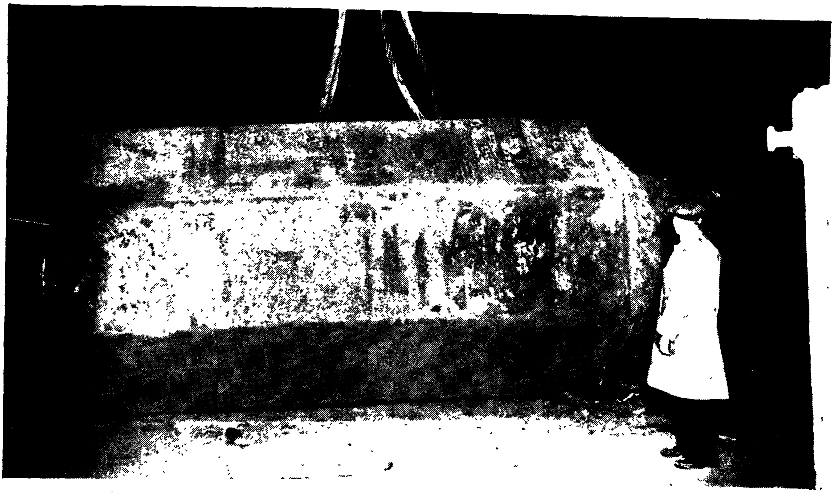

FIG. 269.—175-ton ingot. (English Steel Corporation, Ltd.)

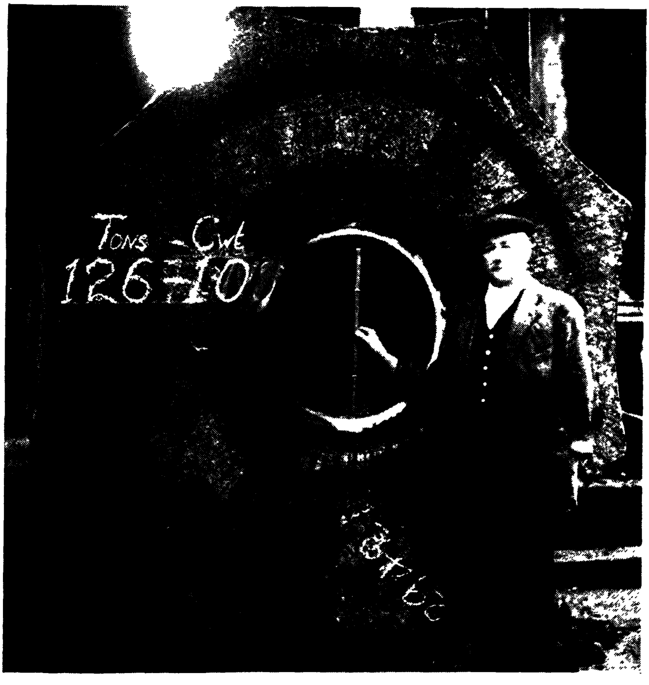

FIG. 270.—Trepanned ingot at the works of Thos. Firth & John Brown, Ltd.

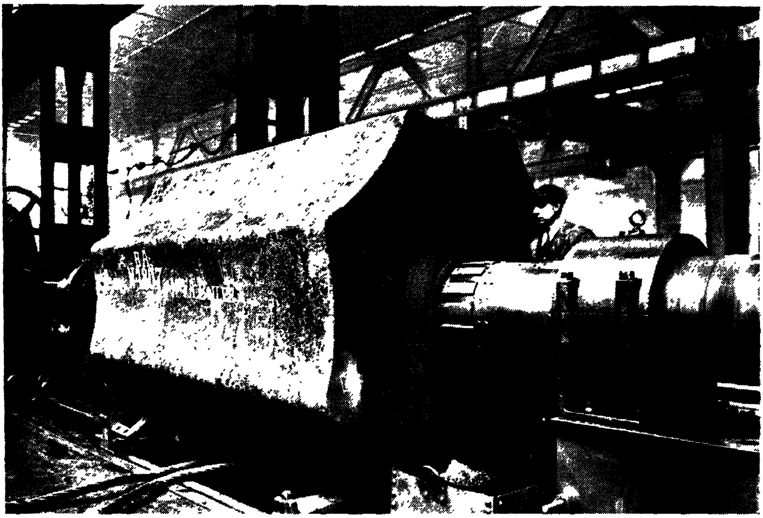

FIG. 271.—Trepanning an ingot at the works of the English Steel Corporation, Ltd.

FIG. 272.—Enlarging the hole of a hollow forging. (English Steel Corporation, Ltd.)

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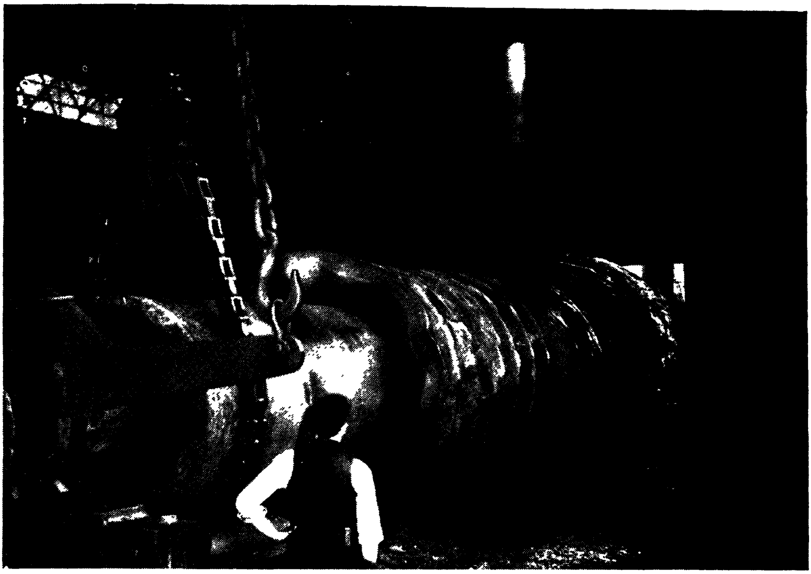

FIG. 273.—Producing a hollow forged cylinder. (English Steel Corporation, Ltd.)

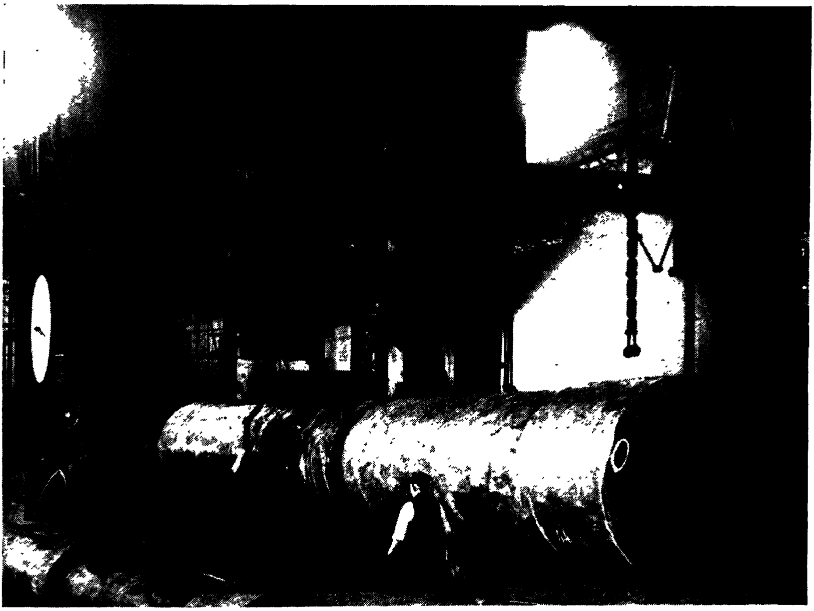

FIG. 274.—Hollow forged boiler drum, 44 ft. long. Weight 100 tons.

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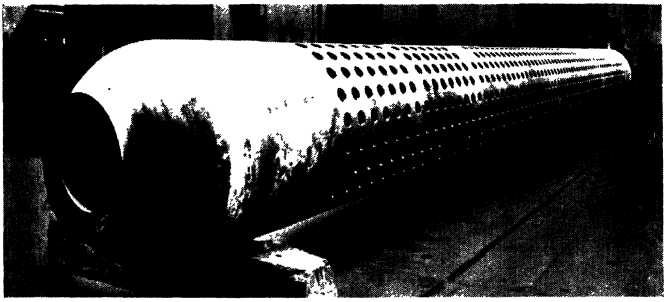

FIG. 275.—Hollow forged steam drum for water-tube boiler. (English Steel Corporation, Ltd.)

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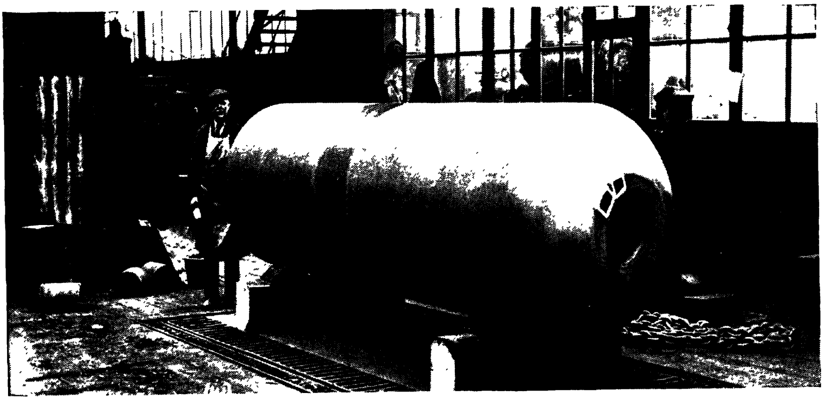

FIG. 276.—Hollow forged steam drum of nickel-chrome-molybdenum steel. (Thos. Firth & John Brown, Ltd.)

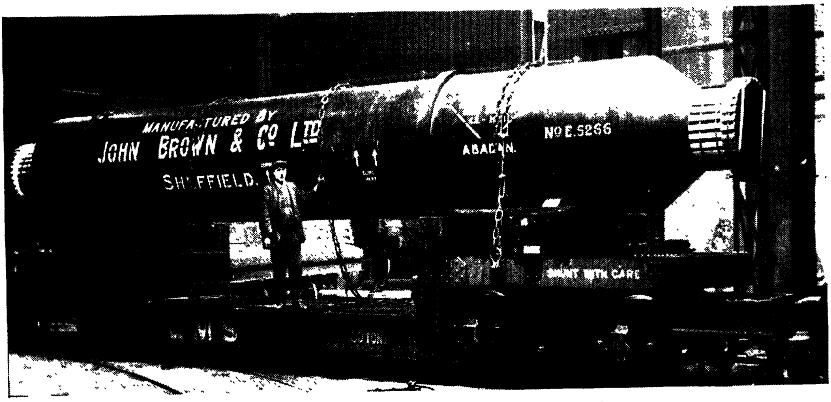

FIG. 277.—Hollow forged reaction vessel.

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sq. in.; the drum is 5-ft. 3-in. internal diameter, wall thickness 4½ ins., length just over 44 ft. and finished weight 55 tons. There are 535 tube holes.

These drums were of carbon steel. An example of a nickel-chromium-molybdenum steel drum, by Thos. Firth & John Brown, Ltd., is shown in Fig. 276. This is 42-in. internal diameter, 15 ft. 7 ins. long, with a wall thickness of 2⅝ ins. for a working pressure 1575 lbs. per sq. in. at 602° F.

A large hollow forged reaction vessel for high temperature service also by Firth & Brown (test pressure 3000 lbs. per sq. in.) is shown in Fig. 277. It is 44 ft. long, 52-in. internal diameter, and 4-in. wall thickness. An even larger hollow forged pressure vessel for use in oil processing is seen in Fig. 278. It is 48 ft. long, 71¼-in. internal diameter, and 2¾-in. wall thickness. It is suitable for working pressures of 400 lbs. per sq. in. at high temperatures (1000° F.). Examples of hollow forged boiler drums are shown in Fig. 279. The smaller drum is for superheated steam at pressures of 1000 lbs. per sq. in. It is 6 ft. 3 ins. long, 23-in. internal diameter, with a wall thickness of 1½ ins.

A large steam drum for a working pressure of 1400 lbs./sq. in., as forged by Thos. Firth & John Brown, Ltd., is seen in Fig. 280. The dimensions are 45 ft. long, 48-in. internal diameter, and 5-in. wall thickness. With the exception of Fig. 276, all the vessels by Firth & Brown are of carbon steel.

Messrs. Thyssen of Mulheim-Ruhr, Germany, have developed a special technique for the manufacture of high-pressure drums and reaction vessels, in which they employ water-gas welding for the longitudinal and circular seams. This process is, of course, considerably cheaper than the hollow forging method just described, as vessels can be made up from standard qualities of thick steel plate, rolled and welded. The actual procedure adopted by Messrs. Thyssen is as follows :—

The welding of the drum longitudinal seams is carried out with a water-gas flame of a reducing nature, and the edges to be welded are worked by means of rolling at welding temperature, so as to avoid altering the structure of the metal as is the case with fusion welding. After welding the drum is annealed and a jam put on the rolls to ensure true circularity, the roll pressure being relieved early enough to prevent rolling at too low a temperature. After completion of the longitudinal seams, these are then closely inspected, and if satisfactory an internal hydraulic pressure of 50 per cent. above the desired working pressure is applied. The ends are then closed in and manhole and other openings fitted. After this operation the drum is then highly stressed by application of an internal hydraulic pressure of three to four times the working pressure. (This operation is very similar to that described in Chapter III., viz. autofrettage, but in the case of these drums the hydraulic pressure is not quite so severe.) After application of this high internal pressure, the drum is heat-treated to relieve internal strains.

During the past nine years, Messrs. Thyssen have made 1000 of such drums, the majority of which were for steam pressures over 500 lbs. per sq. in.

Messrs. Thyssen recommend the following formula for use with their gas-welded vessels :—

S = plate thickness in mm.
D = largest inside diameter of the drum (mm.).
p = working pressure, kg./cm.^{2}
K_z = ultimate strength of the material, kg./mm.^{2}
x = factor of safety, which is usually taken as 4·25.
v = ratio of strength of welded seam to that of solid plate. This is to be taken as 0·9.

Their formula is

$$S = \frac{D \times p \times x}{200 \times K_z \times v} + 1 \; mm.$$

The addition of 1 mm. in the case of a plate thickness of more than 30 mm. may be reduced to 0·5 mm., and over 40 mm. plates may be omitted.

It is to be noted that this formula only applies when the working conditions do not come within the " creep " region, i.e. below 300° C. or so. If above that temperature, due allowance must be made in respect of this important factor in giving a value to K_z and x.

Messrs. Thyssen have very kindly supplied me with the following photographs to illustrate their manufacture of these water-gas welded vessels. These are as follows :—

Fig. 281 shows the plates rolled ready for welding the longitudinal seam.

Fig. 282 shows the actual operation of welding the longitudinal seam of a pressure vessel, in which a water-gas reducing flame is used and the rolling operation during the actual welding is shown in the illustration.

Fig. 283 shows one end of the vessel which has just undergone the closing-in operation and Fig. 284 shows the actual hydraulic pressing operation to close in the end of one of these welded vessels. A completed vessel undergoing hydraulic test is shown in Fig. 285.

Examples of finished water-gas welded vessels are given in the following illustrations :—

Fig. 286 shows a set of starting bottles for Diesel engines. They are used for storing air at pressures of 75 atms. The test pressure

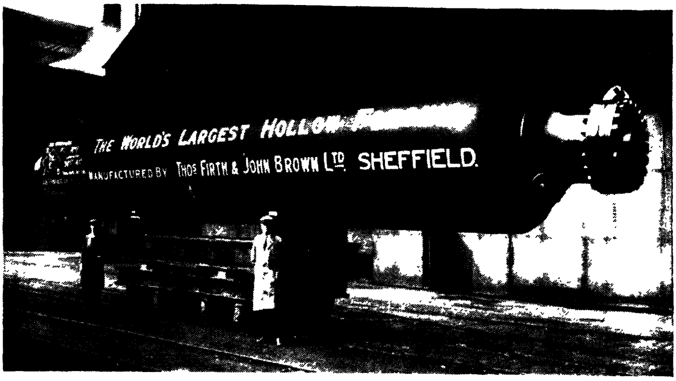
THE WORLD'S LARGEST HOLLOW
MANUFACTURED BY THOS FIRTH & JOHN BROWN LTD. SHEFFIELD.

FIG. 278.—Large hollow forged reaction vessel.

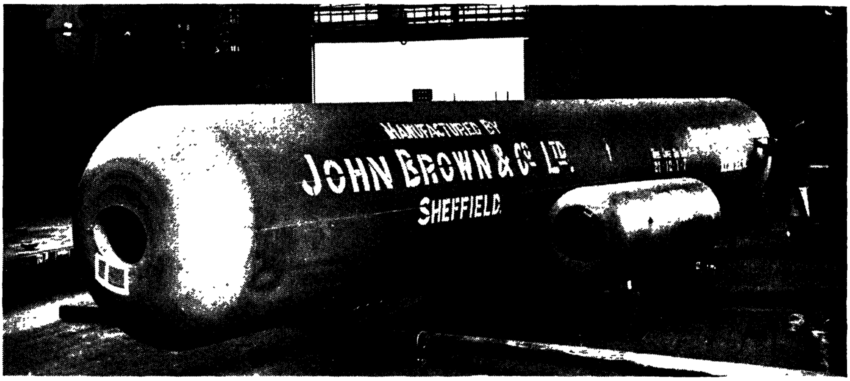

FIG. 279.—Hollow forged boiler drums. (Thos. Firth & John Brown, Ltd.)

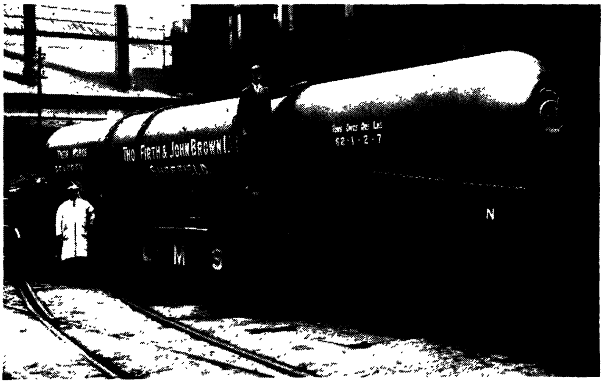

FIG. 280.—1400 lbs. pressure boiler drum. Hollow forged by Thos. Firth & John Brown, Ltd.

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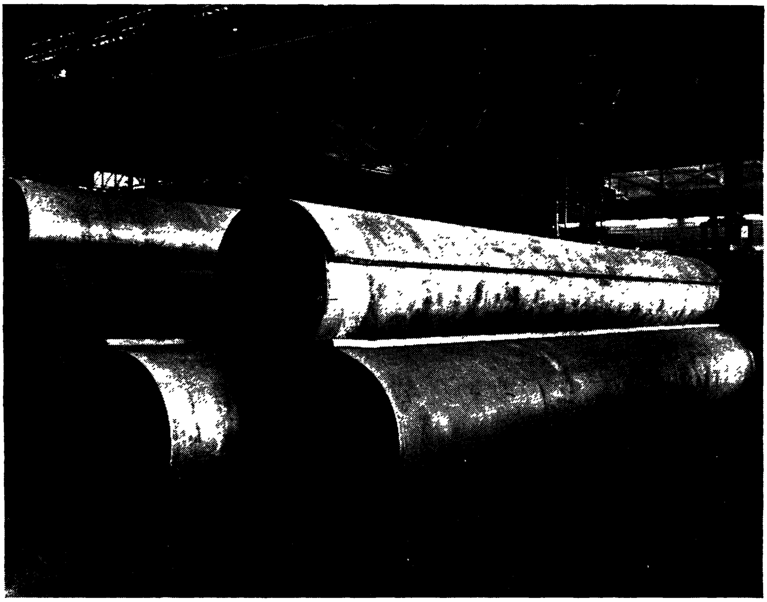

Fig. 281.—Rolled plates ready for welding by the Thyssen water-gas process of pressure vessel construction.

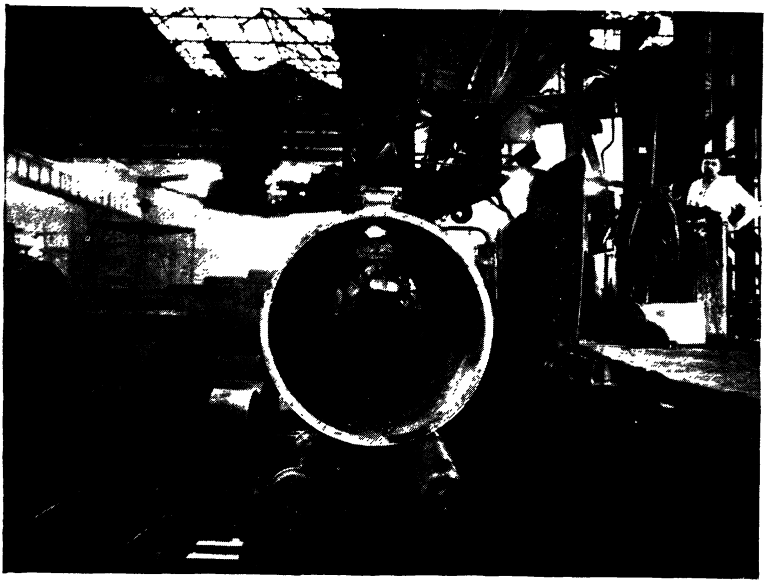

Fig. 282.—Welding the longitudinal seam of a pressure vessel. (Thyssen.)

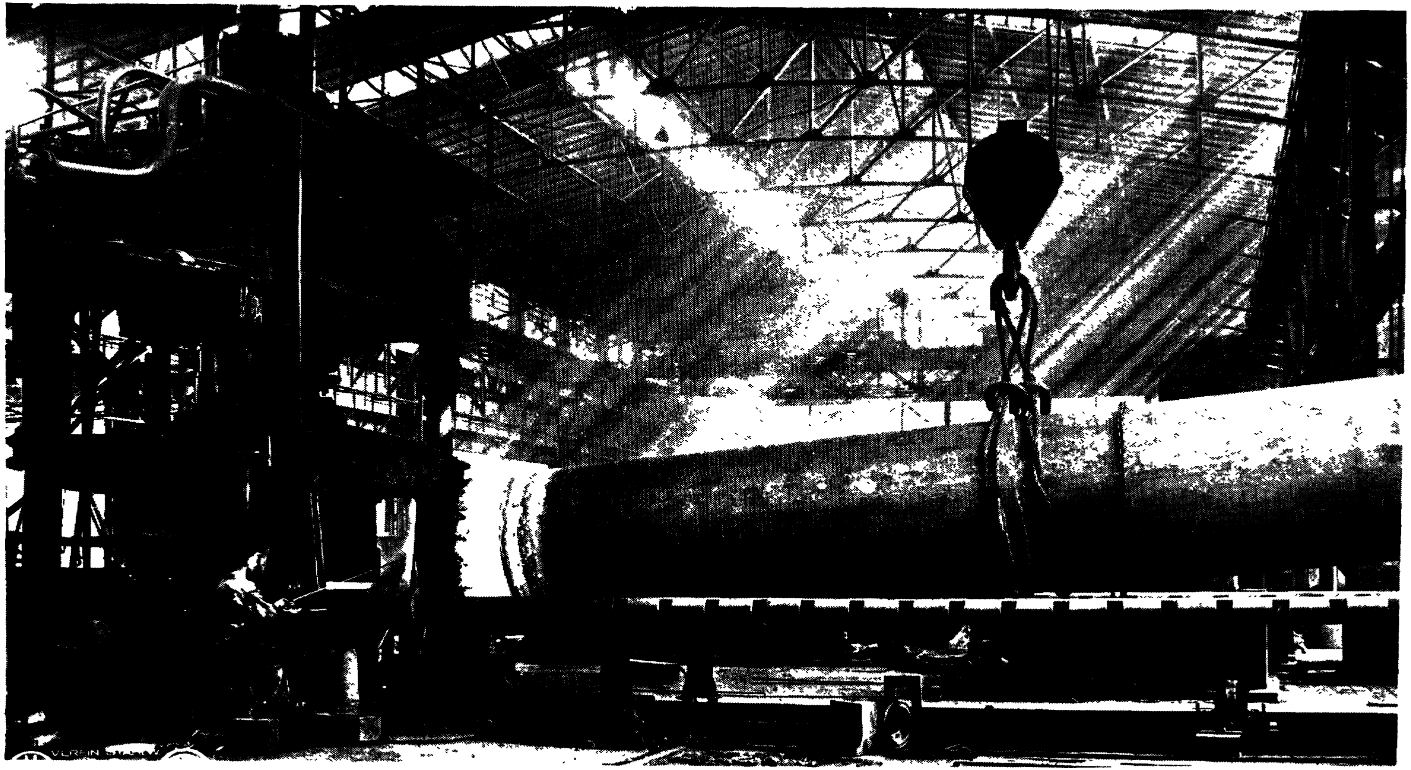

FIG. 283.—Closing the end of a Thyssen water-gas welded vessel.

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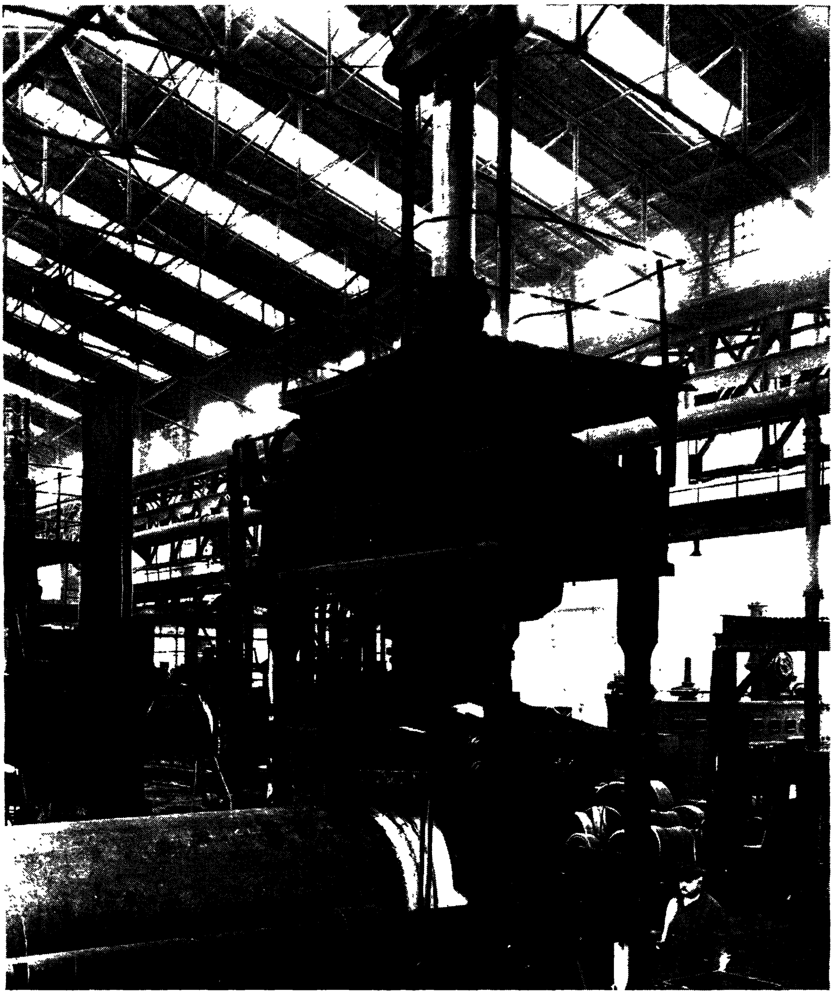

FIG. 284.—Closing the end of a Thyssen water-gas welded vessel.

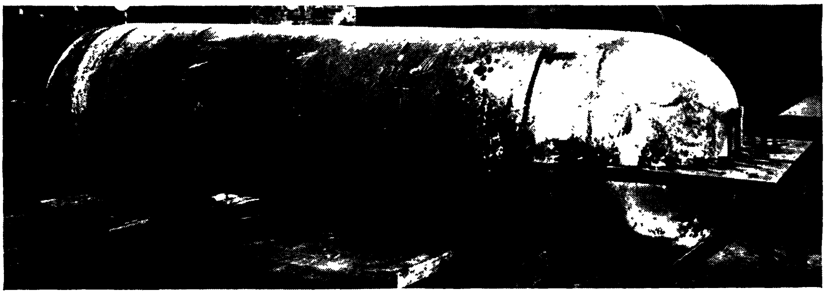

FIG. 285.—Thyssen water-gas welded pressure vessel undergoing hydraulic test.

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was 200 atms. The dimensions of the bottles are as follows : Length, 3040 mm. (10 ft.) ; outside diameter, 800 mm. (31½ ins.) ; wall thickness, 41 mm. (1·6 ins.). Fig. 287 shows a chemical reaction vessel, the dimensions and working pressure of which are given in the figure.

A large chemical autoclave built by Thyssen by their water-gas welding process is shown in Fig. 288. It is fitted with several branches, and is suitable for working pressures of 42 atms. The test pressure was 75 atms. The dimensions of the autoclave are as follows : Length over all, 4860 mm. (16 ft.) ; internal diameter, 1350 mm. (4·5 ft.) ; wall thickness, 47 mm. (about 1⅞ ins.).

Other examples of German technique in the construction of high-pressure vessels are seen in Figs. 289-296 inclusive. (I am indebted to Messrs. Krupp of Essen for permission to publish this information.) Fig. 289 shows a group of large reaction vessels, each 13·42 metres (44 ft. long), with outside diameter of 1·74 metres (5·7 ft.), and wall thickness of 111 mm. (4·37 ins.). They are all hollow, seamless forgings made from Siemens-Martin mild steel, and are suitable for working pressures of 53 atms. at temperatures not exceeding 496° C. The weight of each forging is 58,000 kg. (57 tons).

Another group of large seamless hollow forgings by Krupp is seen in Fig. 290. These are mild steel reaction vessels, and each weighs 100,000 kg. (98 tons). The dimensions are as follows : Length, 15 metres ; inside diameter, 1·5 metres ; and wall thickness, 165 mm. They are designed for a working pressure of 70 atms., at temperatures not exceeding 500° C.

A different type of high-pressure reaction vessel also made by Krupp is seen in Fig. 291. It is again of hollow forged construction, and the ends are sealed by bolted covers. The vessel is for working pressures of 300 atms. at temperatures not exceeding 250° C., and is 7 metres (22·8 ft.) long. The inside diameter is 850 mm. (33·5 ins.), and wall thickness 160 mm. (6·3 ins.). The vessel weighs 33,000 kg., or 32 tons.

Another type of hollow, seamless forging, with one closed end and the other closed by a bolted flange, is shown in Fig. 292. This reaction vessel is made from nickel steel, and it is 1·17 metres (3·84 ft.) inside diameter, with a wall thickness of 160 mm. (6·3 ins.). The weight is 65,000 kg. (63 tons). It is suitable for working pressures of 100-150 atms. at temperatures not exceeding 450° C. The end plate is secured to the body by 16 studs and nuts of chrome-nickel steel, and each stud is 142 mm. (5½ ins.) diameter.

An example of a seamless, hollow forged steam manifold by Krupp is given in Fig. 293. It is for a working pressure of 40 atms. at 450° C., and is made from Siemens-Martin mild steel. The dimensions of the various parts are given in the drawing. A steam drum by Krupp in a special quality of Siemens-Martin mild steel is illustrated in

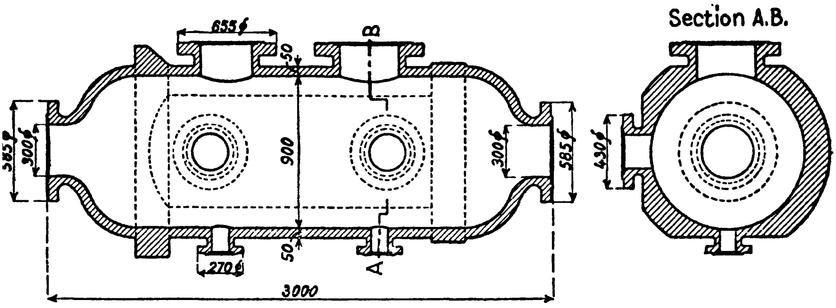

FIG. 293.—Hollow forged, seamless steam manifold. (Fried. Krupp, A.G.)

Fig. 294. It is designed for saturated steam at 100 atms. pressure.

Another hollow forged, seamless steam vessel by Krupp, this time a steam separator, is seen in Fig. 295. It is suitable for a steam pressure of 34 atms. at 450° C. Again the dimensions are given in the illustration.

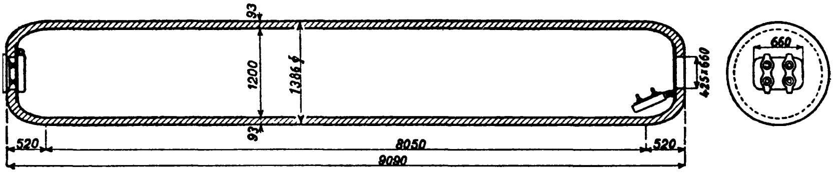

FIG. 294.—Seamless, hollow forged steam drum for 100 atms. (Fried. Krupp, A.G.)

A chemical reaction vessel by Krupp for 1200 atms. working pressure is given in Fig. 296. It is again of hollow forged construction, and is made from chrome-nickel steel, with an ultimate tensile strength of 120 kg./mm.^{2} (or 76 tons/sq. in.).

The old-established Skoda Steel Works of Czechoslovakia also manufacture large hollow forged pressure vessels for the power and chemical industries.

Fig. 297 shows a high-pressure vessel for the synthesis of ammonia, in Siemens-Martin steel. Weight 14 tons; working pressure 4267 lbs. per sq. in; test pressure 7112 lbs. per sq. in. The specification for the steel was: ultimate tensile strength 35/37 tons per sq. in.; yield point 14 tons per sq. in.; elongation 22-24 per cent.

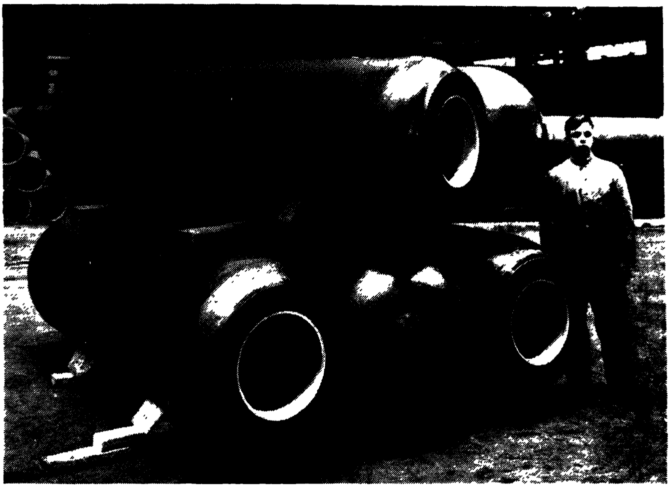

FIG. 286.—Starting bottles for Diesel engines. Made by Thyssen—water-gas welding process.

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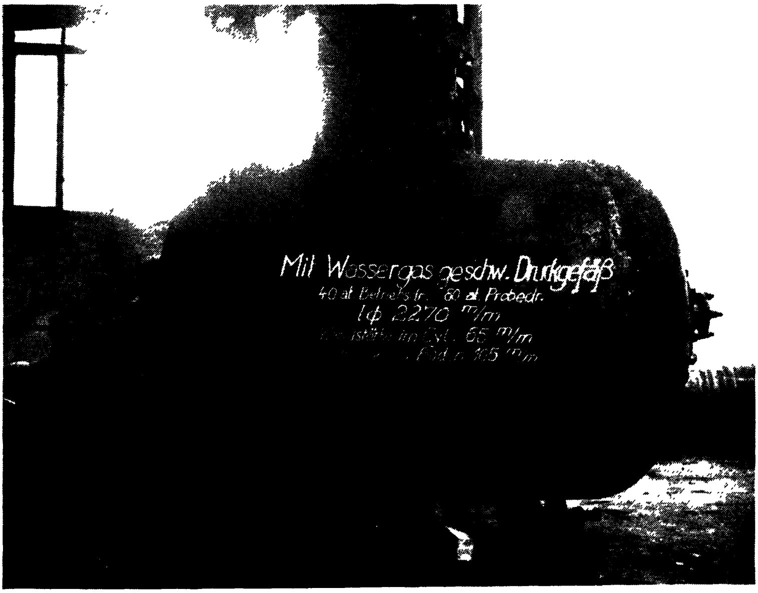
Mit Wassergas geschw. Druckgefäß
40 at Betriebsdr. 60 at Probedr.
lφ 2270 m/m
stärke im Cyl. 65 m/m
Bod. 105 m/m

FIG. 287.—A Thyssen reaction vessel made by the water-gas welding process.

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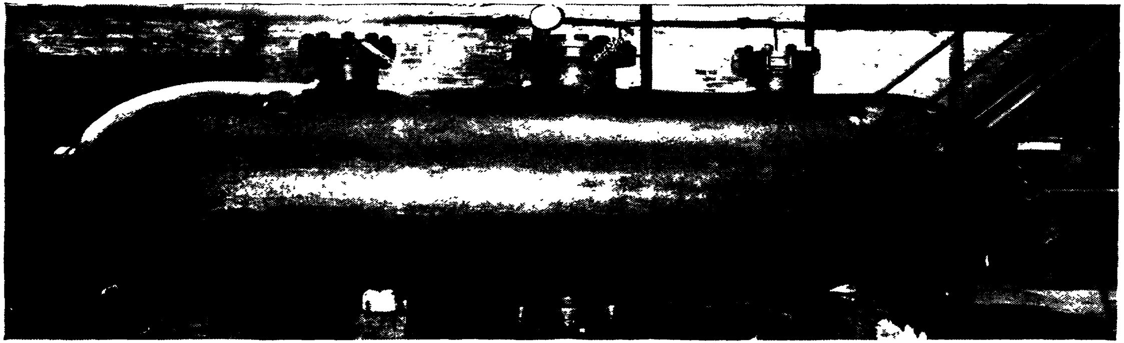

FIG. 288.—Autoclave made by Thyssen water-gas welding process.

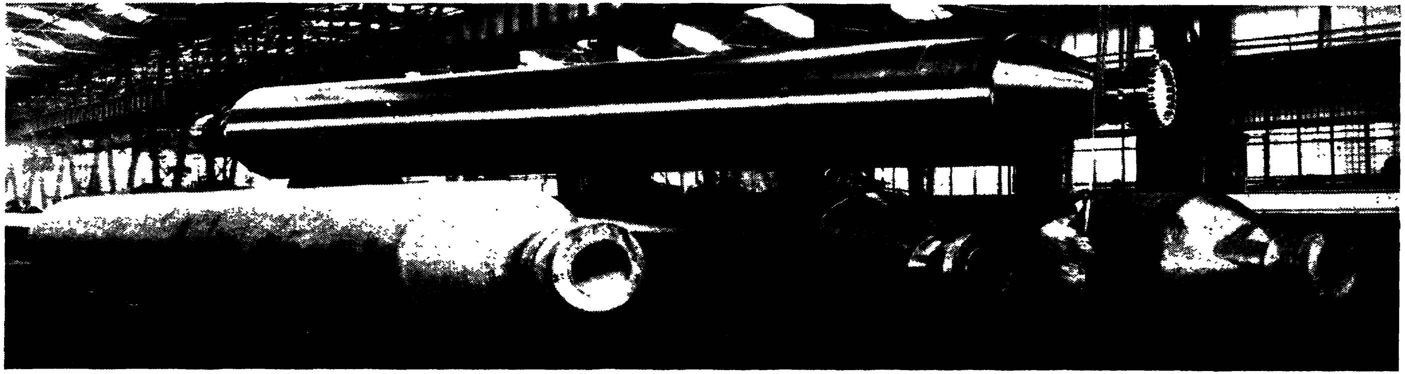

FIG. 289.—Group of large hollow forged reaction vessels. (Fried. Krupp.)

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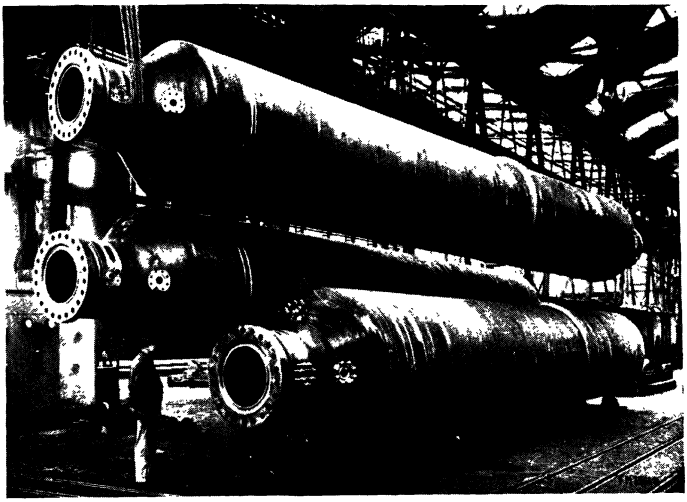

FIG. 290.—Mild steel hollow forged reaction vessels. (Fried. Krupp.)

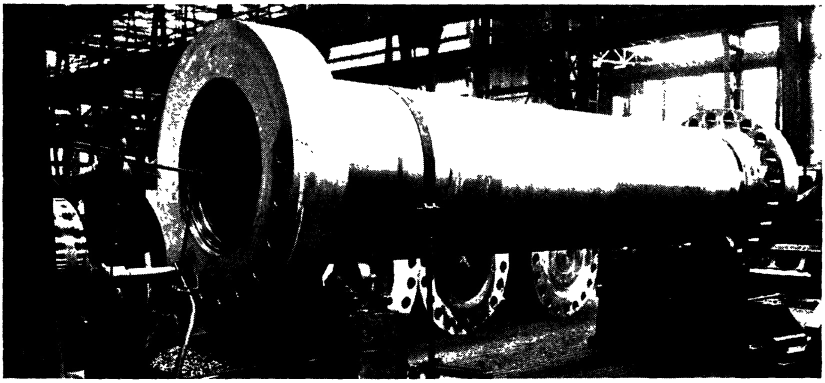

FIG. 291.—Hollow forged reaction vessel. (Fried. Krupp.)

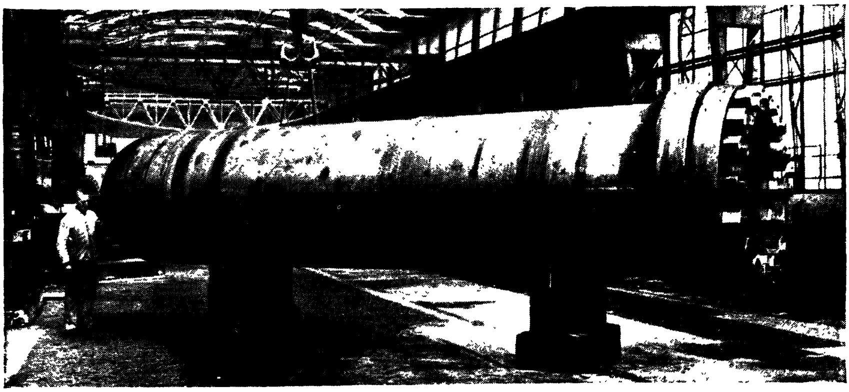

FIG. 292.—Hollow forged reaction vessel. (Fried. Krupp.)

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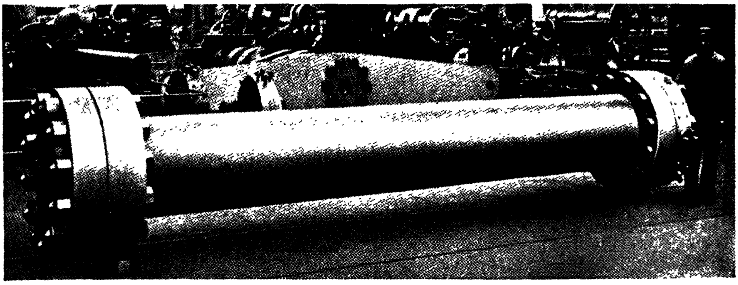

FIG. 297.—Skoda Works: synthetic ammonia catalyst tube.

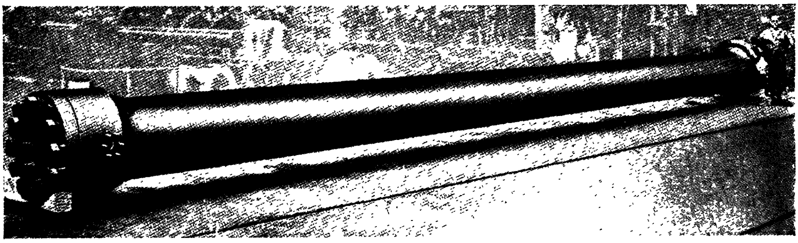

FIG. 298.—Skoda Works: synthetic ammonia catalyst tube.

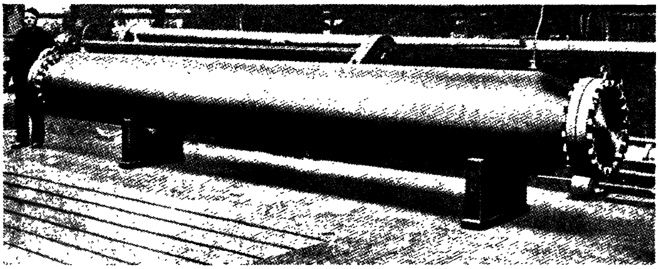

FIG. 299.—Skoda Works: high-pressure reaction vessel for oil refining.

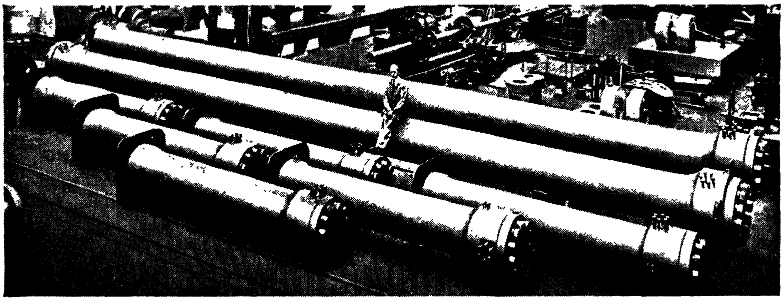

FIG. 300.—Skoda Works: group of vessels for synthetic ammonia plant.

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Another synthetic ammonia vessel by Skoda is shown in Fig. 298. It is in Siemens-Martin steel (annealed). Ult. tensile strength 35 tons per sq. in.; yield point 16·5 tons per sq. in.; elongation 17 per cent. This vessel, which weighs 20 tons, is for a working pressure of 1707 lbs. per sq. in. The test pressure applied was 2560 lbs. per sq. in.

A Skoda high-pressure hollow forged vessel for a crude oil refinery in the Argentine is shown in Fig. 299. It weighs 9 tons and is made from annealed Siemens-Martin steel; ultimate strength 28/32 tons per sq. in.; elongation 22/20 per cent. The operating conditions were 853 lbs. per sq. in., at a temperature of 842-932° F. The test pressure was 2560 lbs. per sq. in.

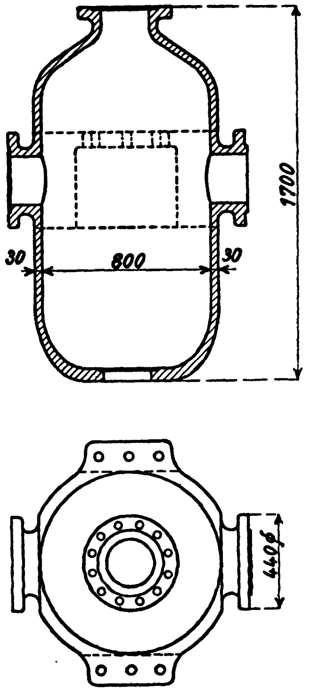

FIG. 295.—Krupp hollow forged high-pressure steam separator.

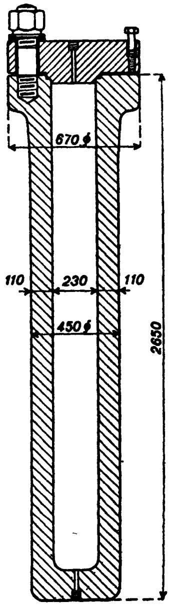

FIG. 296.—Chemical reaction vessel for 1200 atms. (Fried. Krupp, A.G.)

Another group of Skoda hollow forged vessels for synthetic ammonia is shown in Fig. 300. These vessels are made from Siemens-Martin steel (annealed), with an ultimate strength of 35 tons per sq. in.; yield point 16·5 tons per sq. in.; elongation 17 per cent. The working pressure is 1707 lbs. per sq. in. The vessels are 49 ft. 2½ ins. and 13 ft. 1½ ins. long, 19⅝ and 16½ ins. in diameter, and the largest vessel weighs 20 tons.

As will be readily understood, American practice in the construction of chemical pressure vessels has been greatly influenced by the requirements of the petroleum industry. For example, the M. W. Kellogg Co., of Jersey City, N.J., have specialised for many years in the design and construction of pressure plant for this industry, and have developed a special method of electric arc welding with subsequent X-ray inspection of the welded seams.

Figs. 301, 302, 303 illustrate the soaker, evaporator tower and stabiliser tower for the 20,000 b.bl. cracking unit at the Whiting (Indiana) Refinery of the Standard Oil Co. of that State. This is the largest cracking unit ever built, and is practically a complete refinery in itself, as crude oil is charged into the topping end of the unit and stabilised but untreated (70 octane) gasoline is the finished product. The five steps in processing the oil, namely, topping, viscosity breaking, cracking, reforming and stabilising are all done in one unit. This plant was described in Chapter IX.

Referring to Fig. 301, this soaking drum is 10-ft. inside diameter, with 3-in. thick walls, and the complete vessel weighs 309,220 lbs. or about 138 tons. The working pressure is 200 lbs. per sq. in. at 925° F. The vessel is constructed of seamless rolled rings, welded round the circumferential seams.

Fig. 302 shows the evaporator for the Whiting cracking plant and this is constructed from welded plate. It is 12-ft. inside diameter, is just over 48 ft. long, with walls $2\frac{5}{8}$-$3\frac{1}{4}$ ins. thick. The working pressure is 200 lbs. per sq. in. at 825° F. The weight is 285,340 lbs., or just over 125 tons.

The stabiliser tower (Fig. 303) is 6-ft. inside diameter, 85 ft. long, and walls $1\frac{1}{4}$ ins. thick. The working pressure is 300 lbs. per sq. in. at 252° F., and before being put into service it was hydraulically tested to 696 lbs. per sq. in. The tower is made from plate, and is of welded construction throughout.

The scantlings of these vessels include a corrosion allowance sufficient to ensure ten years useful life. This allowance is made in the appropriate dimensions of all Kellogg vessels for such work.

A reaction chamber for the Greybull (Wyoming) Refinery of the Standard Oil Co. of Indiana is shown in Fig. 304. It is 5-ft. inside diameter with walls $4\frac{3}{8}$ ins. thick and is 43 ft. $7\frac{3}{4}$ ins. long overall. It is built from seamless rolled rings with welded circular seams. The ends, ellipsoid in section, are $4\frac{5}{8}$ ins. thick and are welded to the shell. The standpipes and branches are also welded to shell. The vessel is for a working pressure of 750 lbs. per sq. in. at a temperature of 925° F., and before being put into service the vessel was hydraulically tested to 2544 lbs. per sq. in. The finished weight of the vessel is 150,000 lbs., or 67 tons.

Another reaction vessel for petroleum refining is seen in Fig. 305.

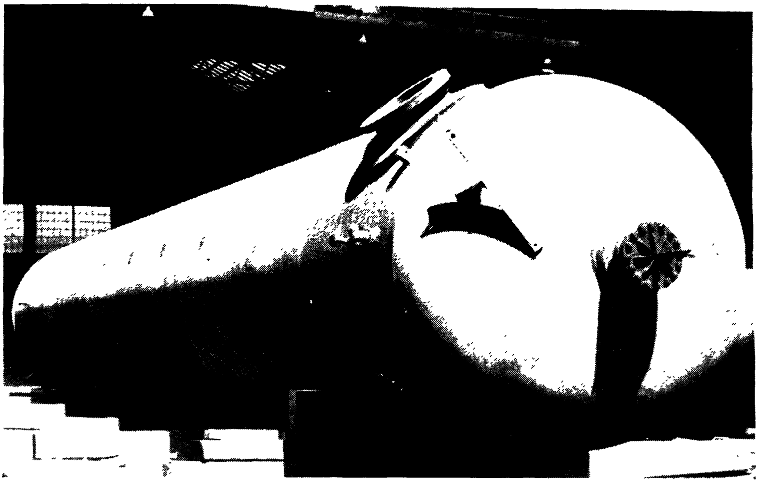

FIG. 301.—Kellogg welded soaking drum for Whiting Refinery of Standard Oil Co.

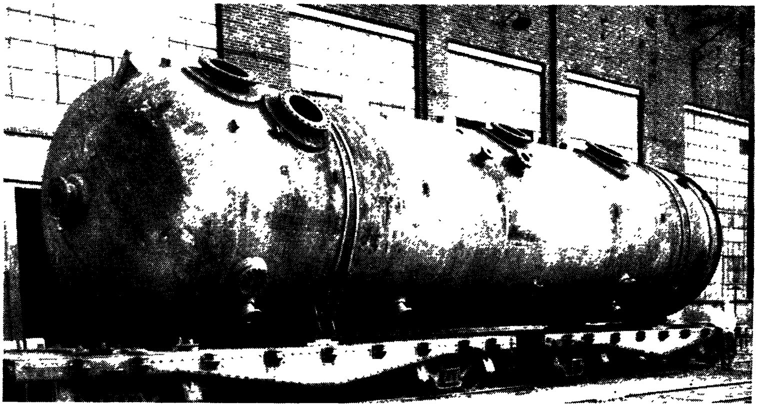

FIG. 302.—Kellogg welded evaporator for Whiting Refinery of Standard Oil Co.

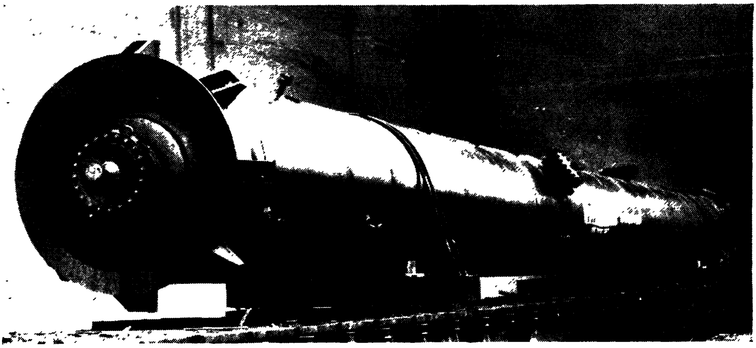

FIG. 303.—Kellogg welded stabiliser tower for Whiting Refinery of Standard Oil Co.

[*To face page* **398.**

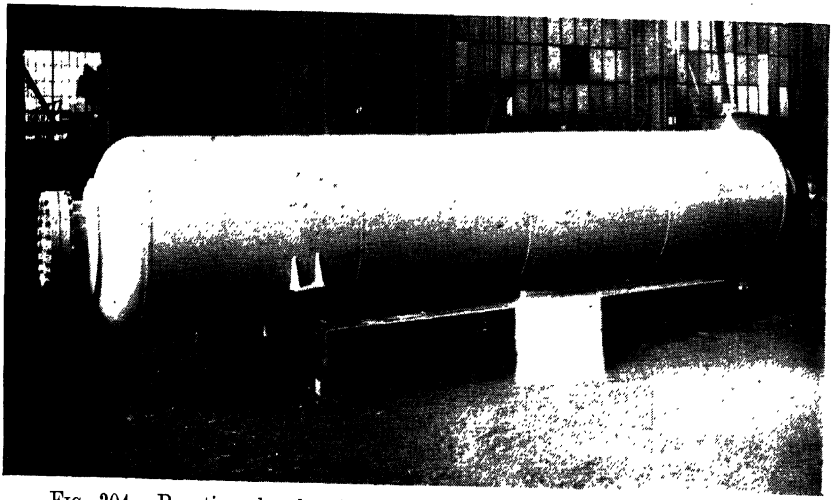

FIG. 304.—Reaction chamber for Greybull (Wyoming) Refinery of Standard Oil Co. Kellogg welded.

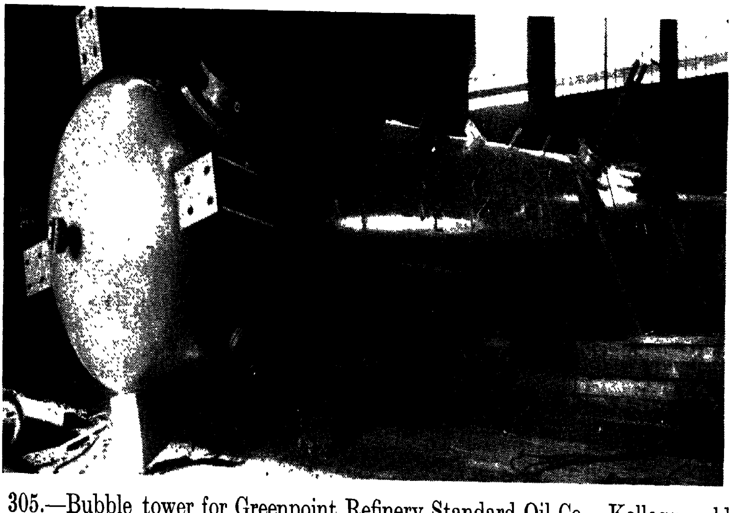

FIG. 305.—Bubble tower for Greenpoint Refinery Standard Oil Co. Kellogg welded.

[*See page* 398.

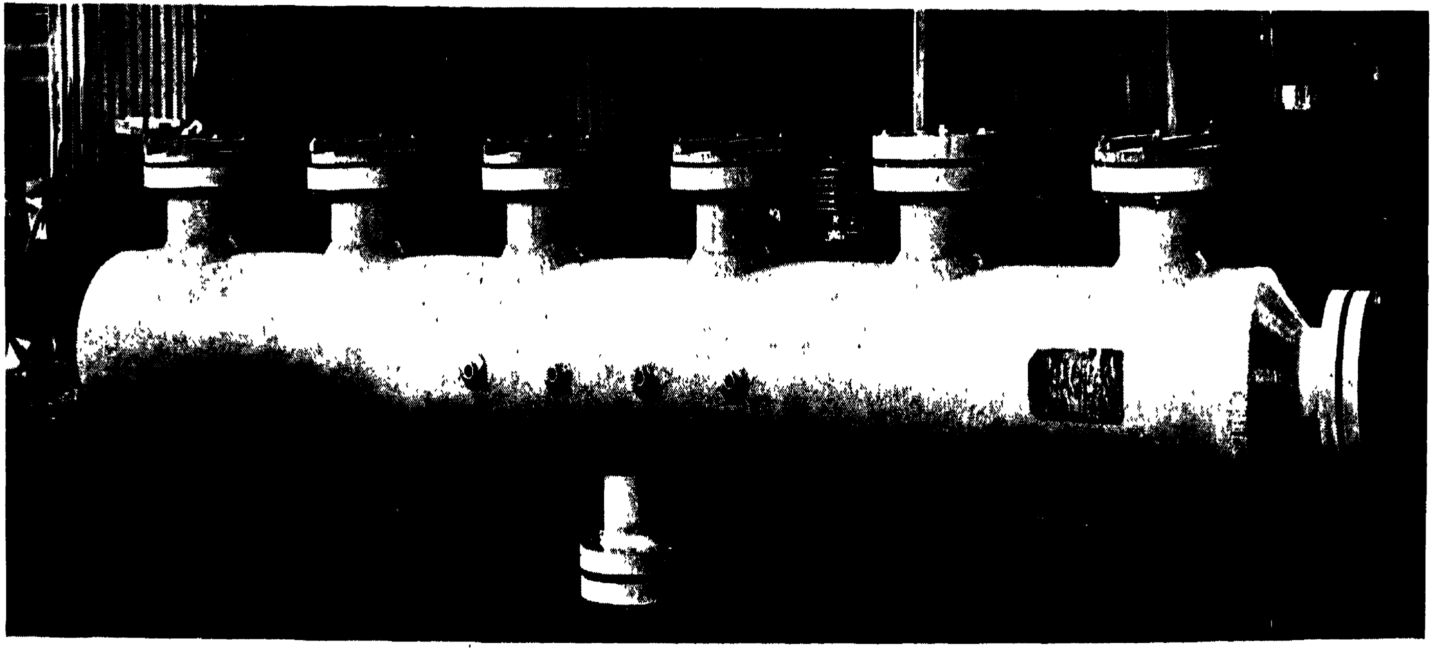

FIG. 306.—Steam manifold. Kellogg masterwelded.

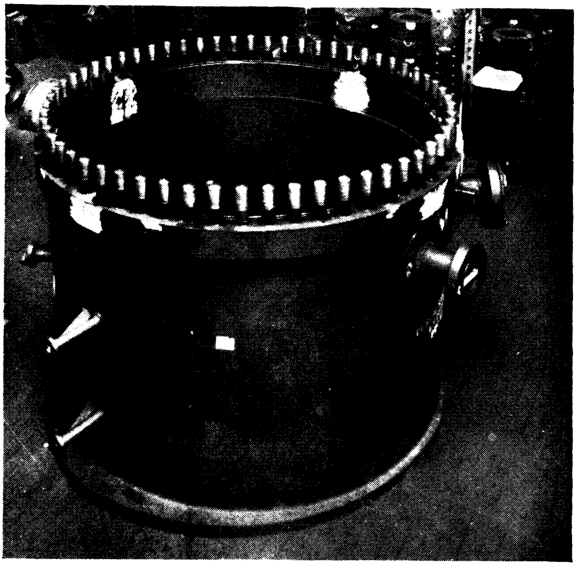

Fig. 307.—Seamless hollow forged ring for mercury vapour boiler. (The Kellogg Co.)

[*To face page* 399.

It is a bubble tower for the Greenpoint (N.Y.) Refinery of the Standard Oil Co. of New York. It is 8-ft. inside diameter, with walls $1\frac{3}{8}$ ins. thick and is 55 ft. $3\frac{3}{8}$ ins. overall. It was built from seamless rolled rings, with welded circular seams. The working pressure is 150 lbs. per sq. in. at 650° F., and before being put into service it was hydraulically tested to 225 lbs. per sq in.

An example of a steam manifold by the Kellogg Co. is given in Fig. 306. It was built up from seamless steel tube 18-in. outside diameter and $\frac{13}{16}$-in. thick, with 7 to 8-in. inside diameter, solid forged standpipes welded on. One end is fitted with an ellipsoid head $\frac{13}{16}$-in. thick and the other is fitted with a reducer 8-in. diameter, both heads welded to the body. The working pressure of this manifold is 400 lbs. per sq. in. at 750° F., and the hydraulic test pressure was 1000 lbs. per sq. in.

An interesting seamless hollow forged ring manufactured by the Kellogg Co. for the General Electric Co. is illustrated in Fig. 307. It is a steam drum for the steam side of a mercury vapour boiler, and is 9-ft. inside diameter, with walls $2\frac{1}{2}$ ins. thick and is 6 ft. $9\frac{1}{4}$ ins. overall. The working pressure is 450 lbs. per sq. in. and the temperature that of saturated steam at this pressure.

APPENDIX.

THE physical properties of gases, liquids and solids when subjected to high pressure are of great interest in many phases of the design of high-pressure plant.

This subject has been investigated by physicists for many years, notably in the earlier stages by Natterer (Gasverdichtungs-Versuche, *Wien*, *Ber.*, **5**, 351-358 (1850); **6**, 557-570 (1851), and **12**, 199-208 (1854); Cailletet, who published a series of papers in *Comptes Rendus*, 1870-1880, and especially Amagat, who also published in *Comptes Rendus* between 1869-1894.

Later Tammann (*Zeit. Phys. Chem.*, 1894-1928), Lussana (*Nuov. Cim.*, 1895-1923), and notably Bridgman (who publishes chiefly in the *Proceedings* of the American Academy of Science) have carried out a great deal of work in this connection, chiefly at very high pressures (3000 atms. and upwards). (See also Bridgman's book, " The Physics of High Pressure," London, G. Bell & Sons, 1931.) Recently Michels of Amsterdam, and Bone of the Imperial College, London, have also entered this field, and the latter is doing a considerable amount of useful work dealing with the compressibilities of gases at industrially useful pressures. Michels and Bone both publish much of their work in the *Proceedings* of the Royal Society.

Critical Data.

The critical temperature, θ_c, is defined as the highest temperature at which a gas can be liquefied by subjecting it to pressure.

The critical pressure, p_c, is the pressure of the gas and liquid at the critical temperature.

The following table gives the above particulars for many substances used in high-pressure investigations :—

Substance.	Critical Temp. θ_c ° C.	Critical Pressure p_c atms.
Hydrogen .	−239·9	12·8
Oxygen . .	−118	50
Nitrogen .	−146	33
Air . .	−140	39
Neon . .	−228·7	26·9
Helium . .	−268	2·26
Krypton . .	− 62·5	54·3
Argon . .	−122	48·0
Xenon . .	14·7	57·2
Chlorine .	144	76
Bromine . .	302	131
Water . .	365	194·6
Carbon monoxide	−141·1	35·9
Carbon dioxide	31·1	73
Ammonia .	130	115
Sulphur dioxide	155·4	78·9
Methane . .	− 82	46
Acetylene	36·5	61·6
Ethylene .	10	51·7
Ethane . .	34	50·2
Methyl alcohol .	240	78·5
Ethyl alcohol .	243	62·7
Ether . .	197	35·8
Chloroform .	260	54·9
Benzene . .	288·5	47·9

Other properties of ammonia and carbon dioxide are given in the following tables :—

PROPERTIES OF ANHYDROUS CARBON DIOXIDE.

Temp. Deg. F.	Absolute Pressure Atmosphere.	Latent Heat of Evaporation. B.Th.U. per lb.	Liquid Heat. B.Th.U. per lb.	Cub. ft. Vapour per lb.	Cub. ft. Liquid per lb.
−22	14·5	126·8	−24·8	·434	·0156
−13	17·0	123·2	−21·1	·368	·0157
− 4	19·7	119·1	−17·2	·313	·0161
5	22·8	115·3	−13·2	·268	·0164
14	26·2	110·6	− 9·0	·230	·0167
23	30·7	105·5	− 4·6	·196	·0172
32	34·3	99·8	0·0	·167	·0177
41	39·8	93·3	4·9	·143	·0181
50	44·2	85·9	10·3	·120	·0188
59	50·7	77·2	16·2	·101	·0198
68	56·3	66·5	23·1	·084	·0210
77	63·8	52·2	31·6	·067	·0230
86	70·7	27·0	45·4	·048	·0268
88·43	—	—	—	·03461	·03461

Properties of Anhydrous Ammonia.

Temp. Deg. F.	Absolute Pressure. Lbs. per sq. in.	Latent Heat of Evaporation. B.Th.U. per lb.	Liquid Heat in B.Th.U. per lb.	Cub. ft. Vapour per lb.
−22	16·95	595·2	−45·92	16·03
−13	21·51	592·4	−38·65	12·85
− 4	27·03	589·0	−31·21	10·37
5	33·68	584·8	−23·63	8·43
14	41·57	580·0	−15·89	6·94
23	50·92	575·0	− 8·05	5·75
32	61·84	569·0	0·00	4·79
41	74·55	562·5	8·17	4·01
50	89·21	555·5	16·51	3·39
59	106·00	547·9	24·97	2·89
68	125·08	539·8	33·59	2·47
77	146·63	531·0	42·35	2·12
86	170·85	521·5	51·28	1·83
95	197·81	511·2	60·34	1·59
104	227·76	500·4	69·55	1·40

Compressibilities of Liquids.

Perhaps the most striking fact in this connection is that the volume changes of widely different liquids appear to approach uniformity at very high pressures, though their compressibility is widely different at lower pressures. It is to be noted that the compressibility of most liquids drops rapidly with increasing pressure.

A good idea of the compressibilities of water, mercury and glycerine over the whole pressure range, 0-12,000 atms., is given in the following table. It is taken from Bridgman's results in this respect :—

Pressure, kg/cm.^{2}	Water. Rel. Vol.			Mercury. Rel. Vol.		Glycerine. Rel. Vol.
	0°.	50°.	95°.	0°.	20°.	30°.
0	1·0000	1·0119	1·0395	1·00000	1·00362	1·000
1,000	0·9567	0·9741	0·9984	0·99626	0·99972	
2,000	0·9248	0·9439	0·9661	0·99261	0·99593	0·958
3,000	0·8996	0·9201	0·9409	0·98905	0·99232	
4,000	0·8795	0·8997	0·9194	0·98561	0·98877	0·932
5,000	0·8626	0·8824	0·9009	0·98231	0·98540	
6,000	—	0·8668	0·8849	0·97914	0·98216	0·911
7,000	—	0·8530	0·8705	0·97607	0·97904	
8,000	—	0·8407	0·8577	—	0·97608	0·893
9,000	—	0·8296	0·8461	—	0·97327	
10,000	—	0·8192	0·8352	—	0·97059	0·879
11,000	—	—	0·8256	—	0·96806	
12,000	—	—	—	—	0·96567	0·866

Compressibility of Gases.

At pressures over 200 atms. or so, even the so-called "permanent" or "perfect" gases begin to deviate markedly from Boyle's Law in respect of volume changes under isothermal compression. For example, the following table illustrates this in the case of nitrogen at 0° C., 50° C., 100° C., and 200° C.:—

VALUES OF PV FOR NITROGEN.

Holborn and Otto.

Pressure Atms.	Temperature °C.			
	0.	50.	100.	200.
1	1·000	1·1837	1·3672	1·7340
30	0·9894	1·1853	1·3768	1·7547
40	0·9870	1·1867	1·3808	1·7622
50	0·9852	1·1886	1·3853	1·7698
60	0·9841	1·1909	1·3899	1·7777
80	0·9836	1·1968	—	—
100	0·9910	—	—	—
200	1·0390	—	1·4890	1·9065
300	1·1360	—	1·5905	2·0145
400	1·2570	—	1·7060	2·1325
500	1·3900	—	1·8275	2·2570
600	1·5260	—	1·9545	2·3840
800	1·7980	—	2·2200	2·6400
1000	2·0685	—	—	—

VALUES OF PV FOR NITROGEN.

Amagat.

Pressure Atms.	0° C.	16° C.	43·6° C.
1	1·0000	—	—
1000	2·0700	2·1340	2·2420
1200	2·3352	2·4000	2·5140
1400	2·5942	2·6558	2·7748
1600	2·8456	2·9088	3·0264
1800	3·0861	3·1536	3·2715
2000	3·3270	3·3980	3·5170
2200	3·5640	3·6366	3·7554
2400	3·8004	3·8724	3·9924
2600	4·0378	4·1054	4·2276
2800	4·2700	4·3386	4·4576
3000	4·4970	4·5675	4·6890

VALUES OF PV FOR NITROGEN AT 68° C.

Bridgman.

p Kgs./sq. cm.	2500.	3000.	4000.	5000.	6000.	7000.	8000.	9000.	10,000.	11,000.	12,000.	13,000.	14,000.	15,000.
pv . .	4·11	4·68	5·82	6·89	7·95	8·95	9·94	10·94	11·91	12·84	13·784	14·70	15·60	16·50

VALUES OF PV FOR OXYGEN.

Holborn and Otto.

Pressure Atm.	Temperature °C.		
	0.	50.	100.
1	1·0000	1·1837	1·3672
30	0·9732	1·1710	1·3638
40	0·9648	1·1673	1·3632
50	0·9568	1·1639	1·3628
60	0·9483	1·1609	1·3627
70	0·9422	1·1582	1·3628
80	0·9375	1·1558	1·3633
100	0·9235	1·1521	—

Amagat.

	0.	15·6.	100.
200	0·9140	0·9945	1·4000
300	0·9625	1·0420	1·4530
400	1·0515	1·1250	1·5320
500	1·1560	1·2270	1·6220
600	1·2690	1·3370	1·7200
800	1·5030	1·5660	1·9340
1000	1·7355	1·7980	2·1510

Values of PV for Oxygen.

Amagat.

P. Atms.	1.	500.	1000.	1200.	1400.	1600.	1800.	2000.	2200.	2400.	2600.	2800.	3000.
0° C.	1·000	1·1570	1·7360	1·9620	2·1798	2·3960	2·6703	2·8160	3·0217	3·2244	3·4229	3·6176	—
15·6° C.	—	—	1·8000	2·0268	2·2470	2·4640	2·6793	2·8880	3·0932	3·2976	3·4996	3·6946	3·8880

PV for Carbon Dioxide.

Amagat.

P. Atms.	0° C.	10° C.	20° C.	30° C.	40° C.	50° C.	100° C.	137° C.	198° C.
1	1·0000	—	—	—	—	—	—	—	—
31	0·7380	—	—	—	—	—	—	—	—
33	0·7120	0·7860	—	—	—	—	—	—	—
34	0·6990	0·7750	—	—	—	—	—	—	—
35	0·0750	0·7640	0·8350	—	—	—	—	—	—
37	0·0790	0·7420	0·8170	0·8820	—	—	—	—	—
40	—	0·7060	0·7895	0·8590	0·9235	—	—	—	—
44	—	0·6530	0·7490	—	—	—	—	—	—
45	—	0·1050	0·7380	0·8190	0·8880	0·9520	—	—	—
48	—	—	0·7060	0·7930	0·8670	0·9330	—	—	—
50	0·1050	0·1145	0·6800	0·7750	0·8500	0·9200	1·2065	1·3800	—
75	0·1530	0·1630	0·1800	0·2190	0·6220	0·7470	1·1180	1·3185	1·6150
100	0·2020	0·2130	0·2285	0·2550	0·3090	0·4910	1·0300	1·2590	1·5820
125	0·2490	0·2620	0·2785	0·3000	0·3350	0·3950	0·9470	1·2050	1·5530
150	0·2950	0·3090	0·3260	0·3460	0·3770	0·4190	0·8780	1·1585	1·5295
175	0·3405	0·3550	0·3725	0·3930	0·4215	0·4570	0·8320	1·1230	1·5100
200	0·3850	0·4010	0·4190	0·4400	0·4675	0·5000	0·8145	1·0960	1·4960
300	0·5595	0·5775	0·5985	0·6225	0·6485	0·6765	0·8900	1·1080	1·4935
400	0·7280	0·7475	0·7710	0·7950	0·8230	0·8515	1·0385	1·2175	1·5630
500	0·8905	0·9130	0·9380	0·9630	0·9900	1·0210	1·2005	1·3620	1·6775
600	1·0495	1·0730	1·0995	1·1275	1·1570	1·1865	1·3655	1·5180	1·8120
700	1·2055	1·2320	1·2590	1·2890	1·3190	1·3500	1·5285	1·6760	1·9560
800	1·3580	1·3870	1·4170	1·4475	1·4790	1·5105	1·6890	1·8355	2·1080
900	1·5090	1·5385	1·5685	1·6000	1·6325	1·6650	1·8460	1·9940	2·2600
1000	1·6560	1·6850	1·7160	1·7480	1·7800	1·8140	1·9990	—	—

PV FOR ETHYLENE.

Amagat.

P. Atms.	0° C.	20° C.	40° C.	60° C.	80° C.	100° C.	137·5° C.	198·5° C.
1	1·0000	—	—	—	—	—	—	—
50	0·1755	0·6290	0·8140	0·9535	1·0770	1·1920	1·3736	1·6520
100	0·3100	0·3600	0·4705	0·6680	0·8465	1·0050	1·2466	1·5800
150	0·4405	0·4850	0·5505	0·6490	0·7760	0·9240	1·1780	1·5400
200	0·5650	0·6095	0·6690	0·7440	0·8380	0·9460	1·1740	1·5368
250	0·6870	0·7325	0·7880	0·8560	0·9370	1·0315	1·2284	1·5690
300	0·8055	0·8520	0·9075	0·9720	1·0475	1·1330	1·3100	1·6276
400	1·0365	1·0840	1·1405	1·2020	1·2725	1·3560	1·5104	1·7900
500	1·2555	1·3075	1·3670	1·4310	1·5000	1·5775	1·7212	1·9846
600	1·4725	1·5250	1·5865	1·6520	1·7215	1·7950	1·9376	2·1910
700	1·6835	1·7375	1·7995	1·8670	1·9365	2·0115	2·1526	2·3990
800	1·8880	1·9460	2·0100	2·0775	2·1495	2·2245	2·3684	2·6060
900	2·0905	2·1530	2·2175	2·2865	2·3595	2·4345	2·5848	2·8140
1000	2·2890	2·3535	2·4215	2·4925	2·5660	2·6425	2·7980	—

PV FOR AIR.

Amagat.

P. Atms.	0° C.	15·7° C.	99·4° C.	200·4° C.
1	1·0000	—	—	—
100	0·9730	1·0460	1·4030	—
150	0·9840	1·0580	1·4310	1·8430
200	1·0100	1·0855	1·4670	1·8860
250	1·0490	1·1260	1·5110	1·9340
300	1·0975	1·1740	1·5585	1·9865
350	1·1540	1·2250	1·6085	2·0410
400	1·2145	1·2835	1·6625	2·0960
450	1·2765	1·3460	1·7200	2·1530
500	1·3400	1·4110	1·7815	2·2110
600	1·4700	1·5375	1·9060	2·3300
700	1·6020	1·6670	2·0300	2·4515
800	1·7345	1·8000	2·1555	2·5750
900	1·8640	1·9300	2·2830	2·7000
1000	1·9920	2·0600	2·4150	2·8280

PV FOR AIR (*cont.*).

Amagat (cont.).

P. Atms.	0° C.	15·7° C.	45·1° C.
1000	1·9990	2·0615	2·1765
1100	2·1329	2·1912	2·3067
1200	2·2596	2·3196	2·4360
1300	2·3842	2·4440	2·5610
1400	2·5081	2·5676	2·6838
1500	2·6310	2·6902	2·8072
2000	3·2260	3·2860	3·4100
2500	3·7912	3·8550	3·9837
3000	4·3230	4·3980	4·5285

PV FOR HYDROGEN AT 65° C.

Bridgman.

P. kg/cm.^{2}	PV.	P. kg/cm.^{2}	PV.
2000	2·54	9,000	7·17
3000	3·18	10,000	7·29
4000	3·83	11,000	7·80
5000	4·50	12,000	8·25
6000	5·08	13,000	8·66
7000	5·65	—	—
8000	6·23	—	—

PV FOR HYDROGEN.

Amagat.

P. Atm.	PV. 0° C.	PV. 15·4° C.	PV. 47·3° C.
1	1·0000	—	—
500	1·3565	—	—
1000	1·7250	1·7780	1·8930
1500	2·0700	2·1270	2·2395
2000	2·3890	2·4450	2·5614
2500	2·6950	2·7525	2·8700
3000	—	3·0375	—

PV FOR HYDROGEN.

Holborn and Otto.

P. Atm.	0° C.	50° C.	100° C.	200° C.
1	1·0000	1·1831	1·3660	1·7317
40	1·0247	1·2094	1·3931	1·7590
80	1·0506	1·2365	1·4209	1·7871
100	1·0638	1·2500	1·4348	1·8011

Amagat.

	0° C.	15·5° C.	100° C.	200° C.
200	1·1380	1·1980	1·5135	1·8840
300	1·2090	1·2685	1·5860	1·9560
400	1·2830	1·3410	1·6590	2·0300

Note.—It is interesting to note that Bridgman found the density of hydrogen was 0·1301 at 15,000 atms. and 65° C. Under similar conditions nitrogen had a density of 1·102.

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